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ELECTRONIC SUPPORTING INFORMATION

Extended Enantiopure o-OPE-based Helical Systems as Scaffolds for Supramolecular Architectures. A Study of Chiroptical Response and its Connection to the CISS effect

Ana M. Ortuño,[a] Pablo Reiné,[a] Sandra Resa,[a] Luis Ávarez de Cienfuegos,[a] Víctor Blanco,[a] José Manuel Paredes,[b] Antonio J. Mota,[*c] Giuseppe Mazzeo,[d] Sergio Abbate,[d] Giovanna Longhi,[*d] Jesús Ugalde,[e] Vladimiro Mujica,[e,f] Delia Miguel[*b] and Juan Manuel Cuerva[*a]

[a.] *Department of Organic Chemistry, University of Granada (UGR). C. U. Fuentenueva, 18071 Granada, Spain. email: jmcuerva@ugr.es*

[b.] *Department of Physical Chemistry. Faculty of Pharmacy. UGR-UEQ. E-mail: dmalvarez@ugr.es*

[c.] *Department of Organic Chemistry. Faculty of Science. UGR-UEQ. E-mail:mota@ugr.es*

[d.] *Department of Molecular and Translational Medicine, Università di Brescia, Brescia, Italy; Istituto Nazionale di Ottica – CNR, Brescia Research Unit, via Branze 45, 25123 Brescia, Italy. E-mail: giovanna.longhi@unibs.it*

[e.] *Kimika Fakultatea, Euskal Herriko Unibertsitatea and Donostia International Physics Center (DIPC), P. K. 1072,20080 Donostia, Euskadi, Spain. E-mail: jesus.ugalde@ehu.eus.*

[f.] *Arizona State University, School of Molecular Sciences, Tempe, AZ 85287, U.S.A. E-mail: vmujica@asu.edu.*

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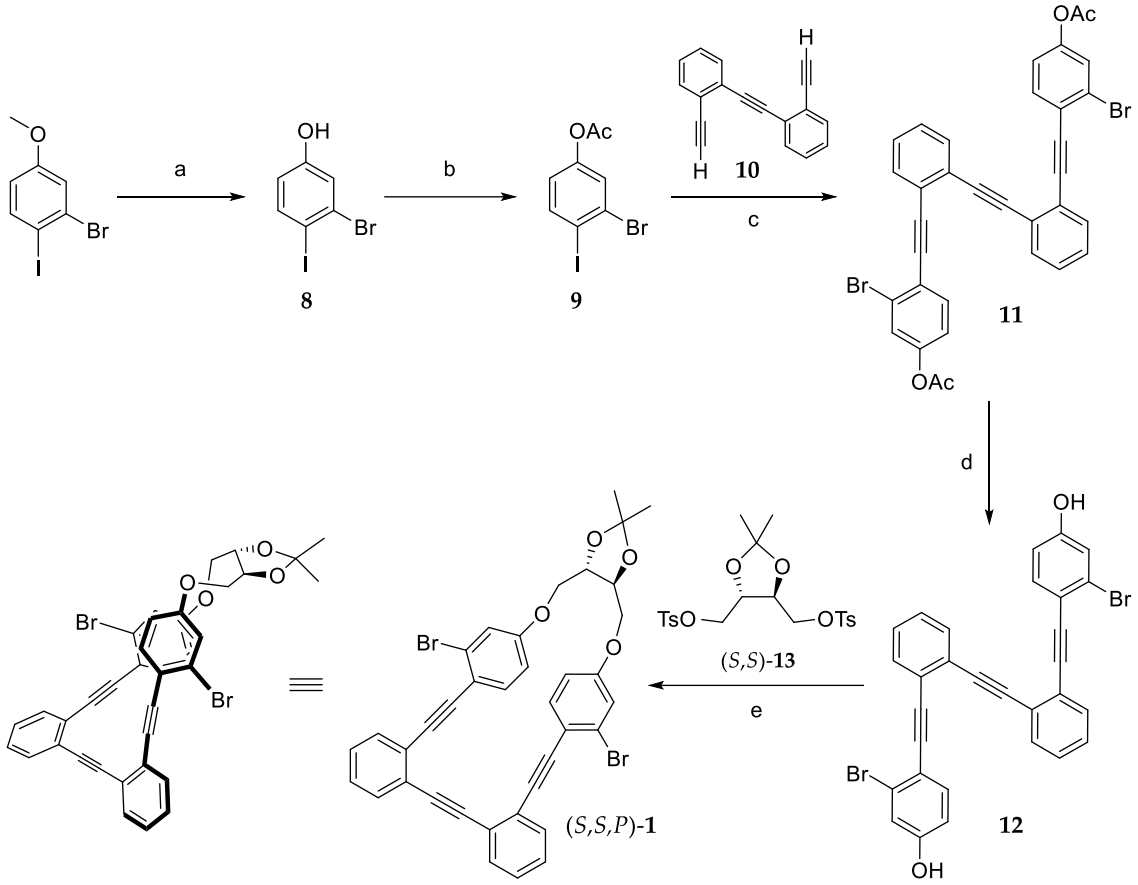
1. SYNTHETIC PART

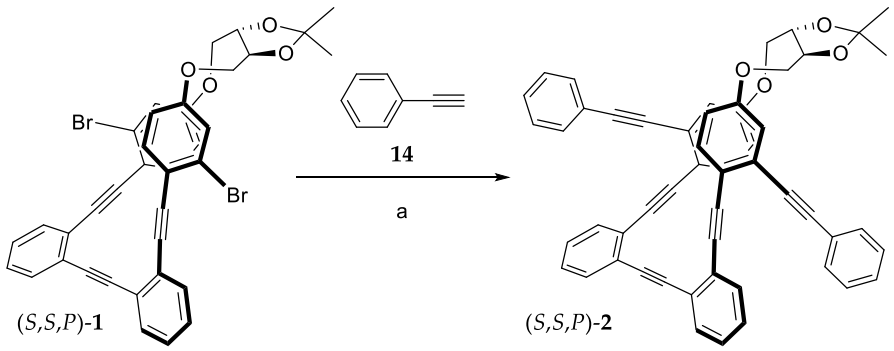
General Details

The following palladium catalysts, trans-dichlorobis(triphenylphosphine) palladium(II) ($Pd(PPh_3)_2Cl_2$) and trans-dichlorobis(acetonitrile)palladium(II) ($Pd(CH_3CN)_2Cl_2$), were prepared from palladium(II) chloride ($PdCl_2$) according to previously described procedures.[1] All reagents and solvents (CH_2Cl_2, EtOAc, Hexane, THF, iPr_2NH, Et_3N, MeOH, CH_3CN) were purchased from standard chemical suppliers and used without further purification. Anhydrous THF was freshly distilled over Na/benzophenone. Thin-layer chromatography analysis was performed on aluminium-backed plates coated with silica gel 60 (230-240 mesh) with F_{254} indicator. The spots were visualized with UV light (254 nm and 360 nm) and/or stained with phosphomolybdic acid (10% ethanol solution) and subsequent heating. Column chromatography purifications were performed with silica gel 60 (40-63 μm). ^1H and ^{13}C NMR spectra were recorded on a Varian Direct Drive (500 MHz) or Bruker Avance Neo (400 MHz or 500 MHz) spectrometers at a constant temperature of 298 K. Chemical shifts are reported in ppm using residual solvent peak as reference ($CDCl_3$: δ = 7.26 ppm, CD_2Cl_2: δ = 5.32 ppm, $(CD_3)_2CO$: δ = 2.05 ppm, DMSO: δ = 2.50 ppm, CD_3OD: δ = 3.31 ppm). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, quint: quintuplet, hept: heptuplet, m: multiplet, dd: doublet of doublets, dt: doublet of triplets, td: triplet of doublets, bs: broad singlet), coupling constant (J in Hz) and integration; ^{13}C NMR spectra were recorded at 101 or 126 MHz using broadband proton decoupling and chemical shifts are reported in ppm using residual solvent peaks as reference ($CDCl_3$: δ = 77.16 ppm, CD_2Cl_2: δ = 54.00 ppm, $(CD_3)_2CO$: δ = 29.84 ppm, DMSO: δ = 39.52 ppm, CD_3OD: δ = 49.00 ppm). Carbon multiplicities were determined by DEPT techniques. High-resolution mass spectra (HRMS) were recorded using EI on a Micromass GCT Agilent Technologies 6890N (Waters), by APCI mass spectra carried out on a Bruker MAXIS II mass spectrometer or by ESI mass spectrometry carried out on a Waters Xevo G2-XS QTof mass spectrometer. The following known compounds were isolated as pure samples and showed NMR spectra identical to reported data: **8**,[2] **10**,[3] **14-18**,[4] **S1**,[5] **S2**,[6] **S3**.[7]

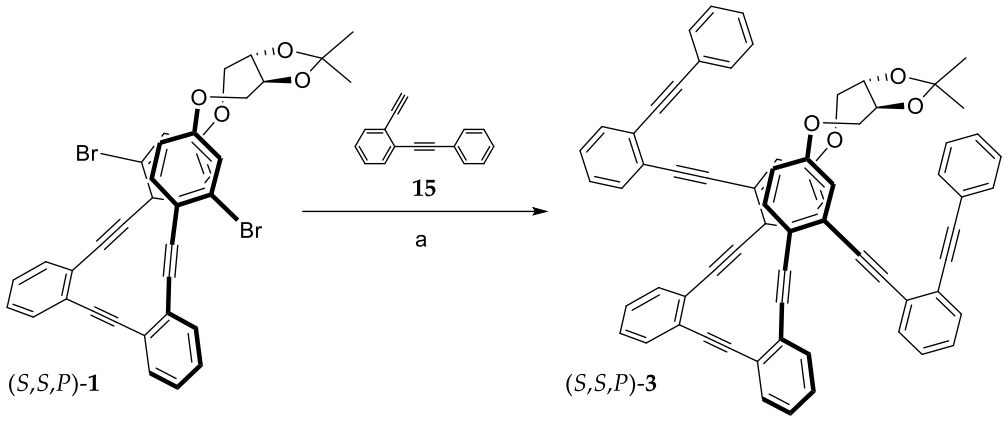
Synthesis and characterization of new compounds



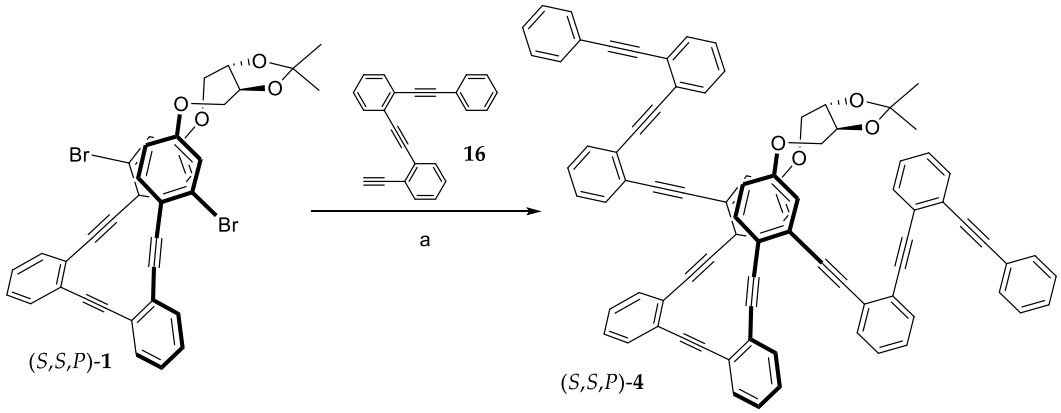
Scheme S1. Synthesis of compound (*S*,*S*,*P*)-**1.** a) BF_3SMe_2, CH_2Cl_2, rt, 6h, 100%. b) Ac_2O, DMAP, CH_2Cl_2, rt, 5 min, 100%. c) $Pd(PPh_3)_2Cl_2$, CuI, 1,2-*bis*(2-ethynylphenyl)ethyne, Et_3N/THF, rt, 24h, 70%. d) K_2CO_3, THF:MeOH (1:1), rt, 30 min, 88%. e) (2S,3S)-(-)-2,3-O-Isopropylidene-1,4-di-O-tosyl-L-threitol, Cs_2CO_3, CH_3CN, reflux, 24h, 56%.



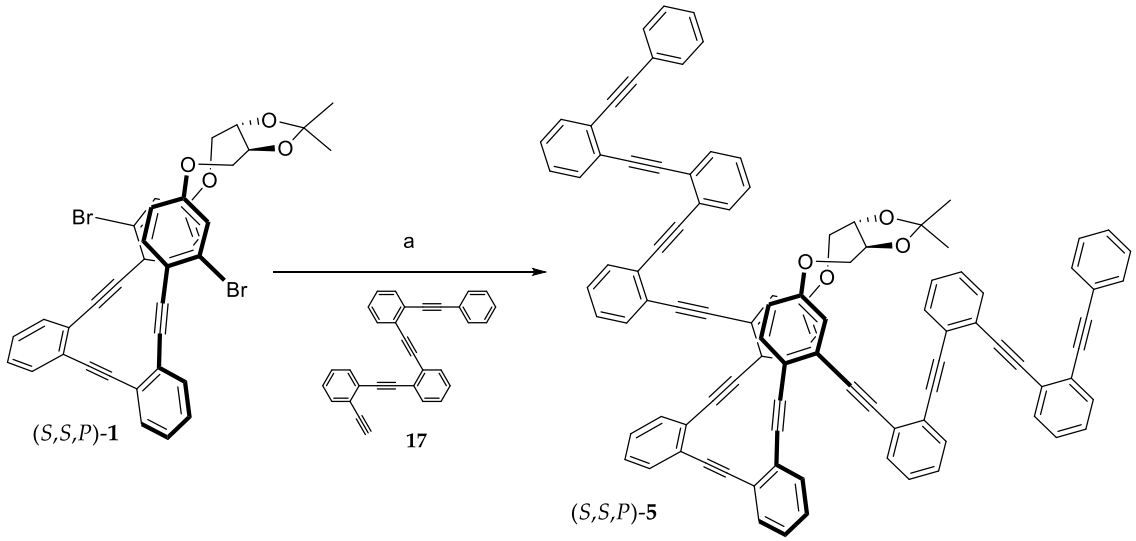
Scheme S2. Synthesis of ligand (*S*,*S*,*P*)-**2.** a) $Pd(CH_3CN)_2Cl_2$, CuI, P*t*Bu_3·HBF_4, *i*Pr_2NH/THF, 60 °C, 24h, 100%.



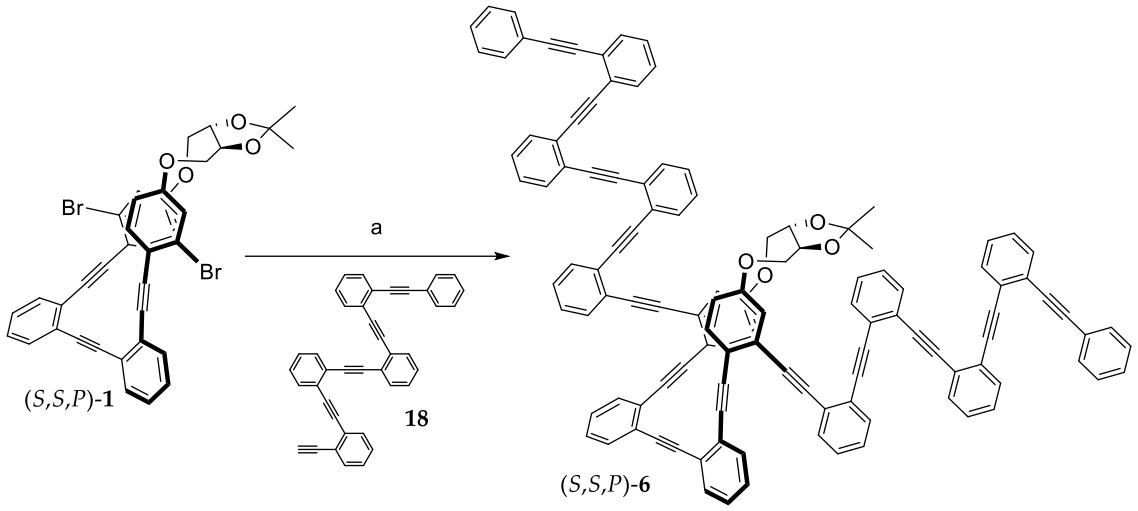
Scheme S3. Synthesis of ligand (*S*,*S*,*P*)-**3.** a) $Pd(CH_3CN)_2Cl_2$, CuI, P*t*Bu$_3$·HBF$_4$, *i*Pr$_2$NH/THF, 60 °C, 24h, 59%.



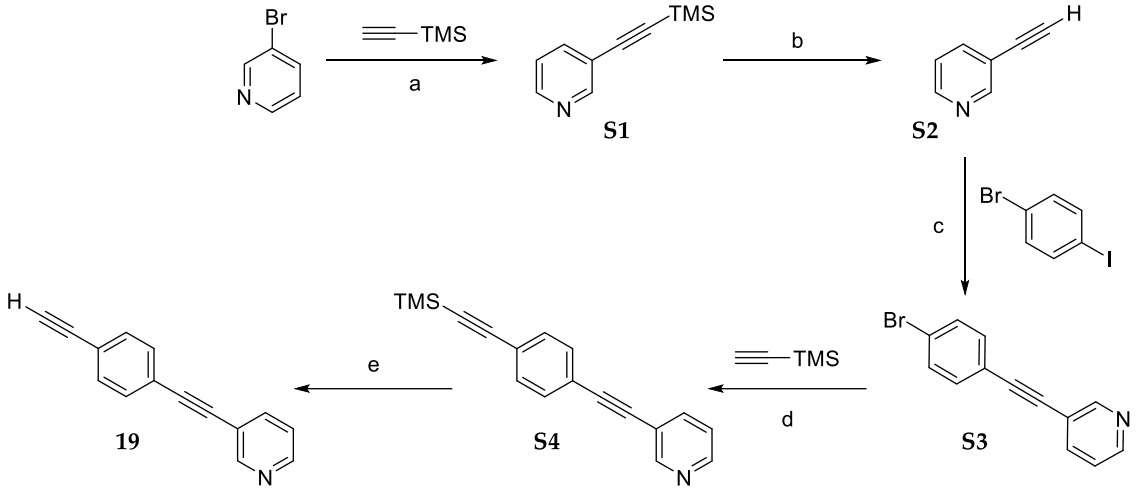
Scheme S4. Synthesis of ligand (*S*,*S*,*P*)-**4.** a) $Pd(CH_3CN)_2Cl_2$, CuI, P*t*Bu$_3$·HBF$_4$, *i*Pr$_2$NH/THF, 60 °C, 24h, 46%.



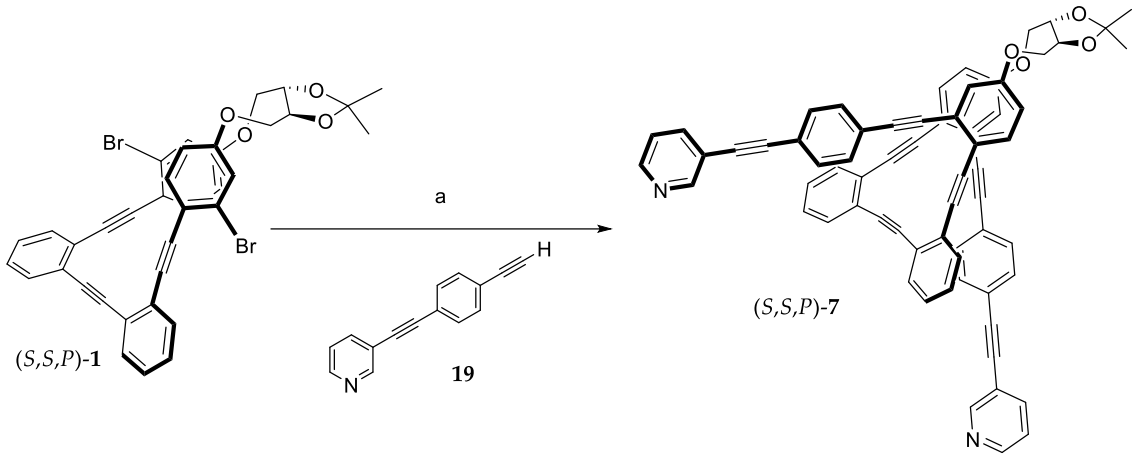
Scheme S5. Synthesis of ligand (*S*,*S*,*P*)-**5.** a) $Pd(CH_3CN)_2Cl_2$, CuI, P*t*Bu$_3$·HBF$_4$, *i*Pr$_2$NH/THF, 60 °C, 24h, 31%.



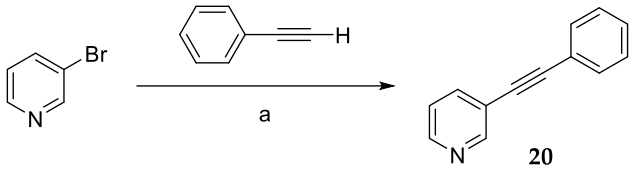
Scheme S6. Synthesis of ligand (*S*,*S*,*P*)-**6.** a) $Pd(CH_3CN)_2Cl_2$, CuI, P*t*Bu_3·HBF_4, *i*Pr_2NH/THF, 60 °C, 24h, 23%.



Scheme S7. Synthesis of compound **19.** a) $Pd(CH_3CN)_2Cl_2$, CuI, P*t*Bu_3·HBF_4, (Triisopropylsilyl)acetylene, *i*Pr_2NH/THF, rt, 3h, 100%. b) Bu_4NF, THF/H_2O, rt, 1h, 80%. c) $Pd(PPh_3)_2Cl_2$, CuI, *p*-bromoiodobenzene, Et_3N/THF, rt, 24h, 92%. d) $Pd(CH_3CN)_2Cl_2$, CuI, P*t*Bu_3·HBF_4, (Triisopropylsilyl)acetylene, *i*Pr_2NH/THF, rt, 24h, 100%. e) K_2CO_3, MeOH, rt, 2h, 100%.



Scheme S8. Synthesis of ligand (*S*,*S*,*P*)-**7.** a) $Pd(CH_3CN)_2Cl_2$, CuI, P*t*Bu$_3$·HBF_4, *i*Pr_2NH/THF, 60 °C, 24h, 81%.



Scheme S9. Synthesis of final model compound **S13.** a) $Pd(CH_3CN)_2Cl_2$, CuI, P*t*Bu$_3$·HBF_4, *i*Pr_2NH/THF, rt, 24h, 100%.

General Procedures

Representative Sonogashira coupling of aryl iodides (GP1). A solution of the terminal alkyne (1.2 mmol to 1.5 mmol per halogen atom) dissolved in the minimum volume of THF and Et_3N (2 mL) was added dropwise to a carefully degassed solution of $Pd(PPh_3)_2Cl_2$ (5 mol%), CuI (10 mol%) and the aryl iodide (1 mmol) in Et_3N (10 mL). The reaction was stirred for 3-24 h at room temperature under argon atmosphere. The mixture was then diluted with EtOAc or dichloromethane (2×20 mL), washed with $NH_4Cl_{(sat.)}$ solution (2×20 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, EtOAc/Hexane mixtures) to give the corresponding coupling product.

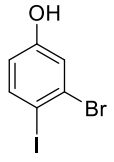
Representative Sonogashira coupling of aryl bromides (GP2). A solution of the terminal alkyne (1.2 to 1.5 mmol per halogen atom) dissolved in the minimum volume of THF and *i*Pr_2NH (2 mL) was added dropwise to a carefully degassed solution of $Pd(CH_3CN)_2Cl_2$ (3 mol%), P*t*Bu$_3$·HBF_4 (6 mol%), CuI (3 mol%) and the aryl bromide (1 mmol) in *i*Pr_2NH (10 mL). The reaction was stirred between 3-24 h at room temperature under argon atmosphere. The mixture was then diluted with EtOAc or

dichloromethane (2×20 mL), washed with saturated aq NH_4Cl solution (2×20mL), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, EtOAc/Hexane mixtures) to give the corresponding coupling product.

Representative protocol for the removal of protecting silyl groups (GP3). To a solution of the starting silyl derivative (1 mmol) in MeOH (10 ml), K_2CO_3 (0.2 mmol) was added, and the mixture was stirred at room temperature until complete consumption of the starting material was determined by TLC (usually 2-3 h). The solvent was removed under reduced pressure and the residue was extracted with water (10 ml) and ethyl acetate (3×10 ml). The combined organic layers were washed with NH_4Cl (2×10 ml) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO_2, EtOAc/Hexane mixtures) to give the pure product.

*Synthesis of (S,S)-**1***

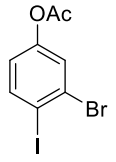
Compound 8



8

The desprotection of 3-bromo-4-iodoanisole was carried out following the protocol established by Moore and collaborators.[8] 4-Bromo-3-iodoanisole (0.97 mL, 6.39 mmol) was dissolved in dry CH_2Cl_2 (15 mL) and $BF_3{\cdot}S(CH_3)_2$ (2.02 mL, 19.17 mmol) was added over 1 min. This mixture was stirred for 6 h, then the solvent was removed under a stream of argon. The residue was partitioned between EtOAc (20 mL) and $HCl_{(aq)}$ (2M, 20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, Hexane/EtOAc, 95:5) yielded 4-bromo-3-iodophenol (**8**) (1.91 g, 100%) as off-white needles. This compound was characterized by NMR and data were identical to those previously reported.[2] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, *J* = 8.6 Hz, 1H), 7.16 (d, *J* = 2.8 Hz, 1H), 6.54 (dd, *J* = 8.6, 2.8 Hz, 1H), 5.31 (s, 1H).

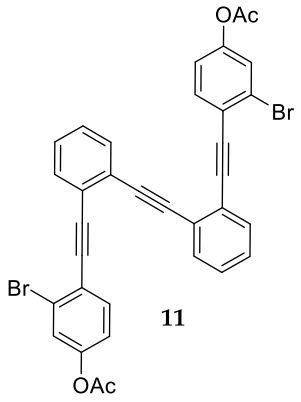
Compound 9



9

DMAP (1.50 g, 12.27 mmol) was added to a solution of **8** (1.91 g, 6.39 mmol) in CH_2Cl_2 (30mL). Acetic anhydride (0.88 mL, 9.2 mmol) was added then over 1 min. The reaction is stirred for 5 min at room temperature. Afterwards, the compound was supported on celite and purified by flash column chromatography (SiO_2, Hexane/EtOAc, 9:1 with Et_3N (1 mL each 250 mL of eluent) to give **9** (2.17 g, 100%) as a yellow liquid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.84 (d, *J* = 8.6 Hz, 1H), 7.41 (d, *J* = 2.6 Hz, 1H), 6.80 (dd, *J* = 8.6, 2.6 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 168.8(C), 151.1(C), 140.6(CH), 130.1(C), 126.3(CH), 122.4(CH), 21.1(CH_3). **HRMS (GC-EI+):** *m*/*z* $[M]^+$ calcd for $C_8H_6O_2BrI$: 339.8596; found: 339.8608.

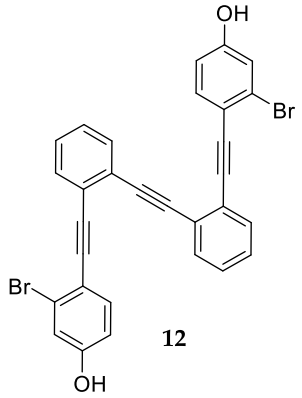
Compound 11



11

11 was prepared from **9** (2.17 g, 6.39 mmol) and **10** (578 mg, 2.50 mmol) according to the previously described *GP1* for 24h to give **11** (2.91 g, 70%) as a dark liquid.. A part of the starting material **9** was recovered in the flash column chromatography and resubmitted to reaction to give overall 91% (3.78 g) of **11**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 – 7.60 (m, 4H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.35 – 7.32 (m, 6H), 6.98 (dd, *J* = 8.5, 2.3 Hz, 2H), 2.29 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.8(C), 150.5(C), 134.1(CH), 132.5(CH), 132.4(CH), 128.5(CH), 128.3(CH), 125.9(C), 125.8(CH), 125.7(C), 125.5(C), 123.2(C), 120.7(CH), 92.8(C), 92.4(C), 91.5(C), 21.2(CH_3). **HRMS (ESI):** *m*/*z* $[M+Na]^+$ calcd for $C_{34}H_{20}Br_2O_4Na$: 674.9606; found: 674.9602.

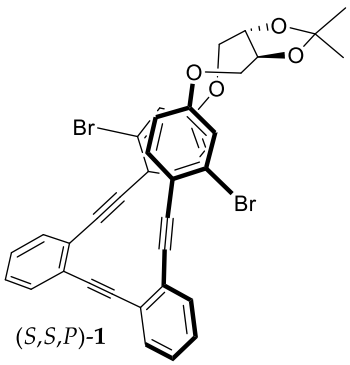
Compound 12



12

To a solution of **11** (2.91 g, 4.46 mmol) in THF/MeOH (1:1) (20 ml), K_2CO_3 (4.31 g, 31.23 mmol) was added, and the mixture was stirred at room temperature until complete consumption of the starting material (30 min). HCl (10%) was added to neutralise the remaining K_2CO_3. Afterwards, the solution was diluted with CH_2Cl_2 (25 mL), washed with HCl (10%) (2×25 ml), dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO_2, Hexane/EtOAc, 7:3) to give **12** (2.23 g, 88%) as a black liquid. **^{1}H NMR (400 MHz, CD_3OD)** δ 7.65 – 7.59 (m, 4H), 7.44 – 7.35 (m, 6H), 7.04 (d, *J* = 2.4 Hz, 2H), 6.71 (dd, *J* = 8.5, 2.4 Hz, 2H). **^{13}C NMR (101 MHz, MeOD)** δ 159.9(C), 135.7(CH), 133.3(CH), 132.9(CH), 129.4(CH), 129.0(CH), 127.3(C), 126.9(C), 126.6(C), 120.3(CH), 117.2(C), 115.8(CH), 93.6(C), 93.1(C), 91.3(C). **HRMS (ESI-):** *m*/z $[M-H]^+$ calcd for $C_{30}H_{15}Br_2O_2$: 564.9439; found: 564.9441.

Compound (*S*,*S*)-1



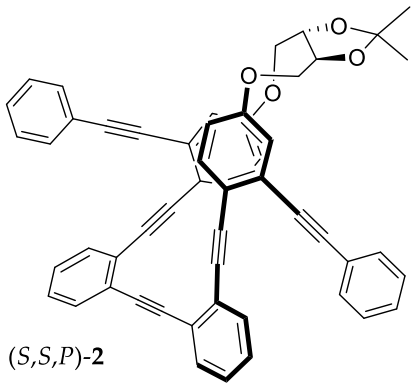
(*S*,*S*,*P*)-**1**

(2S,3S)-(-)-2,3-O-Isopropylidene-1,4-di-O-tosyl-L-threitol (1.84 g, 3.92 mmol) and Cs_2CO_3 (3.06 g, 9.41 mmol) was added to a 250 mL two neck round-bottomed flask under argon atmosphere. A solution of compound **12** (2.23 g, 3.92 mmol) dissolved in CH_3CN dry (120 mL) was added then. The mixture was stirred with reflux during 24 h. Afterwards, the mixture was supported on celite and the solvent

was removed under reduced pressure. The residue was purified by flash column chromatography (SiO_2, Hexane/EtOAc, 8:2) to give a mixture of (*S*,*S*,*P*)-**1** and L-threitol as a yellow solid. To separate them, a precipitation method was used. The solid was dissolved in the minimun ammount of CH_2Cl_2 and hexane was added to precipitate (*S*,*S*,*P*)-**1** (1.52 g, 56%) as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (m, 4H), 7.37 – 7.28 (m, 4H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 2.6 Hz, 2H), 6.28 (dd, *J* = 8.6, 2.6 Hz, 2H), 4.33 – 4.26 (m, 6H), 1.51 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1(C), 134.1(CH), 133.7(CH), 133.4(CH), 128.3(CH), 128.1(CH), 126.9(C), 125.1(C), 124.9(C), 118.3(C), 117.4(CH), 114.4(CH), 109.8(C), 92.5(C), 92.4(C), 91.9(C), 74.8(CH), 67.2(CH_2), 27.0(CH_3). **HRMS (ESI):** *m*/*z* $[M+Na]^+$ calcd for $C_{37}H_{26}Br_2O_4Na$: 715.0096; found: 715.0084.

*Synthesis of ligands (S,S,P)-**2-6***

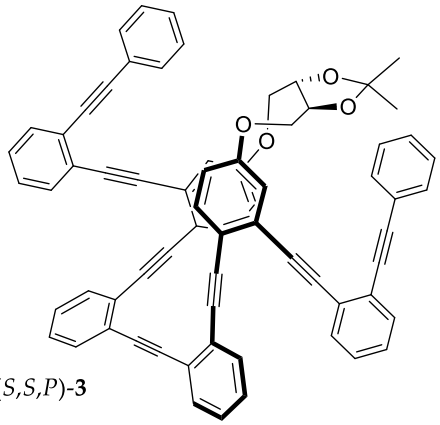
Compound (*S*,*S*,*P*)-2



(*S*,*S*,*P*)-**2**

It was prepared from (*S*,*S*,*P*)-**1** (100 mg, 0.14 mmol) and phenylacetylene (31 μL, 0.43 mmol) according to previously described *GP2* for 24h to give (*S*,*S*,*P*)-**2** (105 mg, 100%) as a yellowish solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.58 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.50 (dd, *J* = 6.6, 1.4 Hz, 6H), 7.27 – 7.24 (m, 4H), 7.19 (tt, *J* = 7.6, 1.6, 0.9 Hz, 4H), 7.13 (tt, *J* = 7.6, 7.1, 1.3 Hz, 4H), 6.81 (d, *J* = 2.7 Hz, 2H), 6.37 (dd, *J* = 8.6, 2.7 Hz, 2H), 4.40 – 4.37 (m, 4H), 4.33 – 4.29 (m, 2H), 1.53 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.48 (C), 133.71 (CH), 133.65 (CH), 133.36 (CH), 132.04 (CH), 128.25 (CH), 128.12 (CH), 128.03 (CH), 127.68 (CH), 127.26 (C), 125.58 (C), 124.96 (C), 123.34 (C), 119.14 (C), 116.47 (CH), 115.21 (CH), 109.62 (C), 93.87 (C), 92.88 (C), 92.69 (C), 91.43 (C), 88.42 (C), 74.99 (CH), 66.96 (CH_2), 27.01 (CH_3). **HRMS (ESI):** *m*/*z* $[M]^+$ calcd for $C_{53}H_{36}O_4$: 759.2511; found: 759.2509.

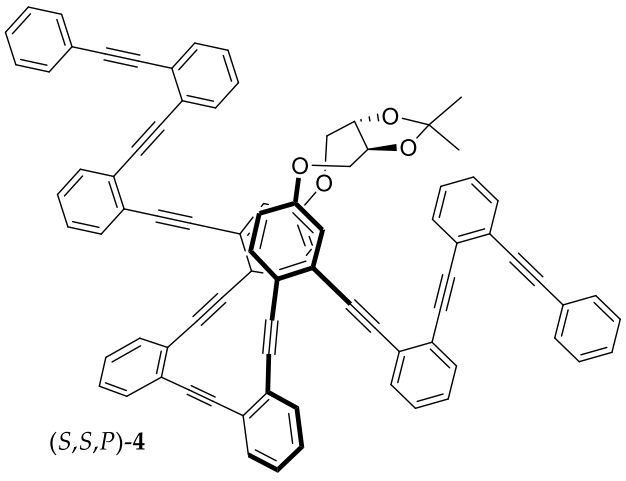
Compound (*S*,*S*,*P*)-3



(*S*,*S*,*P*)-**3**

It was prepared from (*S*,*S*,*P*)-**1** (135 mg, 0.19 mmol) and **S7** (118 mg, 0.58 mmol) according to previously described *GP2* for 24h to give (*S*,*S*,*P*)-**3** (110 mg, 59%) as a yellowish solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.58 – 7.53 (m, 6H), 7.50 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.45 (ddd, *J* = 7.8, 3.3, 1.3 Hz, 4H), 7.34 – 7.27 (m, 6H), 7.22 – 7.10 (m, 8H), 7.03 (td, *J* = 7.7, 1.4 Hz, 2H), 6.77 (d, *J* = 2.7 Hz, 2H), 6.25 (dd, *J* = 8.7, 2.7 Hz, 2H), 4.29 – 4.26 (m, 2H), 4.20 – 4.13 (m, 4H), 1.50 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.37 (C), 133.88 (CH), 133.46 (CH), 133.39 (CH), 132.52 (CH), 131.83 (CH), 131.58 (CH), 128.47 (CH), 128.41 (CH), 128.01 (CH), 127.87 (CH), 127.77 (CH), 127.52 (CH), 127.18 (C), 125.97 (C), 125.79 (C), 125.60 (C), 124.96 (C), 123.54 (C), 119.08 (C), 116.67 (CH), 115.30 (CH), 109.51 (C), 93.57 (C), 92.81 (C), 92.64 (C), 92.59 (C), 92.48 (C), 91.67 (C), 88.69 (C), 74.93 (CH), 66.84 (CH_2), 26.99 (CH_3). **HRMS (ESI):** *m*/*z* $[M+Na]^+$ calcd for $C_{69}H_{44}O_4$: 959.3137; found: 959.3139.

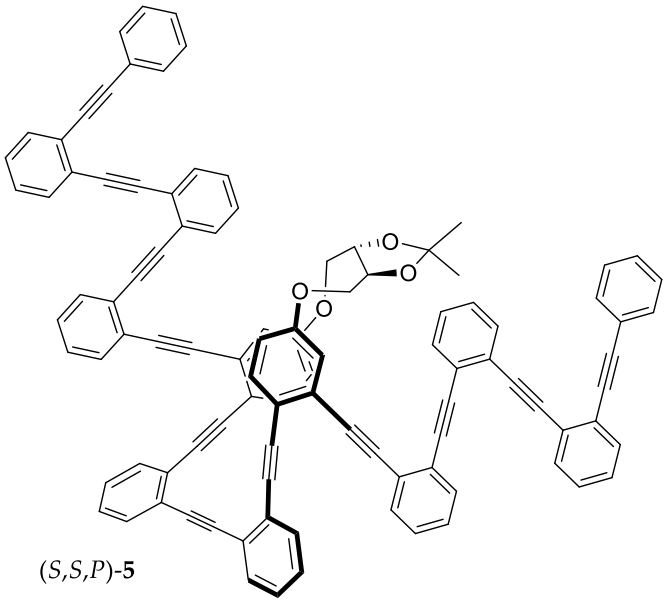
Compound (*S*,*S*,*P*)-4



(*S*,*S*,*P*)-**4**

It was prepared from (*S*,*S*,*P*)-**1** (135 mg, 0.19 mmol) and **S8** (176 mg, 0.58 mmol) according to previously described *GP2* for 24h to give (*S*,*S*,*P*)-**4** (104 mg, 46%) as a yellowish solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.63 – 7.57 (m, 4H), 7.58 – 7.53 (m, 4H), 7.55 – 7.49 (m, 2H), 7.48 (dd, *J* = 7.8, 1.3 Hz, 4H), 7.41 (dd, *J* = 7.8, 1.3 Hz, 2H), 7.32 – 7.25 (m, 11H), 7.20 – 7.11 (m, 5H), 7.13 – 7.06 (m, 2H), 7.04 (td, *J* = 7.6, 1.3 Hz, 2H), 6.72 (d, *J* = 2.7 Hz, 2H), 6.10 (dd, *J* = 8.6, 2.7 Hz, 2H), 4.24 – 4.18 (m, 2H), 4.13 – 4.08 (m, 4H), 1.49 (s, 6H).**^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.30 (C), 133.86 (CH), 133.41 (CH), 133.36 (CH), 132.49 (CH), 132.31 (CH), 131.88 (CH), 131.77 (CH), 128.52 (CH), 128.47 (CH), 128.45 (CH), 128.18 (CH), 128.14 (CH), 127.96 (CH), 127.94 (CH), 127.82 (CH), 127.45 (CH), 127.02 (C), 126.18 (C), 126.01 (C), 125.82 (C), 125.79 (C), 125.58 (C), 124.92 (C), 123.42 (C), 118.98 (C), 116.93 (CH), 115.19 (CH), 109.44 (C), 93.90 (C), 92.90 (C), 92.79 (C), 92.68 (C), 92.65 (C), 92.48 (C), 92.28 (C), 91.54 (C), 88.59 (C), 74.98 (CH), 66.82 (CH_2), 27.00 (CH_3). **HRMS (ESI):** *m*/*z* $[M+Na]^+$ calcd for $C_{85}H_{52}O_4$: 1159.3763; found: 1159.3799.

Compound (*S*,*S*,*P*)-5

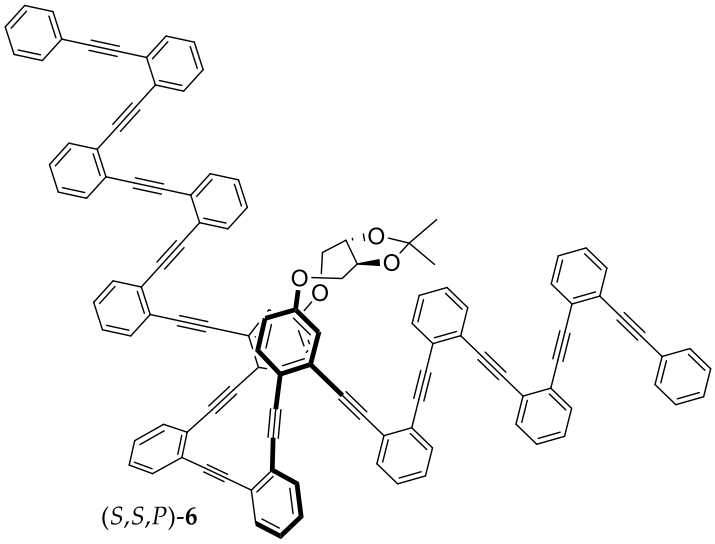


(*S*,*S*,*P*)-**5**

It was prepared from (*S*,*S*,*P*)-**1** (100 mg, 0.14 mmol) and **S9** (232 mg, 0.58 mmol) according to previously described *GP2* for 24h to give (*S*,*S*,*P*)-**5** (60 mg, 31%) as a yellowish solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.63 – 7.58 (m, 4H), 7.58 – 7.50 (m, 8H), 7.47 (d, *J* = 7.8 Hz, 4H), 7.43 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.28 (m, 6H), 7.27 – 7.21 (m, 10H), 7.17 – 7.07 (m, 8H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.72 (s, 2H), 6.06 (d, *J* = 8.6 Hz, 2H), 4.22 (bsignal, 2H), 4.17 – 4.08 (m, 4H), 1.40 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.37 (C), 133.69 (CH), 133.44 (CH), 133.36 (CH), 132.47 (CH), 132.39 (CH), 132.02 (CH),

131.90 (CH), 131.85 (CH), 128.51 (CH), 128.46 (CH), 128.36 (CH), 128.28 (CH), 128.16 (CH), 128.14 (CH), 127.95 (CH), 127.90 (CH), 127.85 (CH), 127.48 (CH), 127.04 (C), 126.09 (C), 125.97 (C), 125.94 (C), 125.79 (C), 125.57 (C), 124.90 (C), 123.43 (C), 118.87 (C), 116.69 (CH), 115.45 (CH), 109.32 (C), 93.77 (C), 92.97 (C), 92.84 (C), 92.67 (C), 92.66 (C), 92.61 (C), 92.41 (C), 92.31 (C), 91.55 (C), 88.59 (C), 74.87 (CH), 66.82 (CH_2), 26.89 (CH_3). **HRMS (ESI):** *m*/*z* $[M+Na]^+$ calcd for $C_{101}H_{60}O_4$: 1359.4389; found: 1359.4474.

Compound (*S*,*S*,*P*)-6

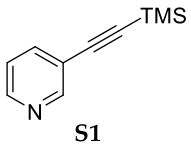


(*S*,*S*,*P*)-**6**

It was prepared from (*S*,*S*,*P*)-**1** (100 mg, 0.14 mmol) and **S10** (290 mg, 0.58 mmol) according to previously described *GP2* for 24h to give (*S*,*S*,*P*)-**6** (51 mg, 23%) as a brown solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.65 – 7.61 (m, 2H), 7.59 – 7.50 (m, 15H), 7.49 – 7.45 (m, 3H), 7.43 (dd, *J* = 7.3, 1.4 Hz, 2H), 7.30 – 7.20 (m, 19H), 7.20 – 7.05 (m, 9H), 7.02 (td, *J* = 7.6, 1.4 Hz, 2H), 6.71 (d, *J* = 2.6 Hz, 2H), 6.05 (dd, *J* = 8.6, 2.6 Hz, 2H), 4.23 – 4.18 (m, 2H), 4.15 – 4.09 (m, 4H), 1.38 (s, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 157.37 (C), 133.72 (CH), 133.44 (CH), 133.35 (CH), 132.52 (CH), 132.39 (CH), 132.33 (CH), 132.24 (CH), 132.21 (CH), 132.16 (CH), 132.02 (CH), 131.90 (CH), 131.84 (CH), 128.49 (CH), 128.41 (CH), 128.32 (CH), 128.26 (CH), 128.08 (CH), 128.06 (CH), 127.96 (CH), 127.88 (CH), 127.86 (CH), 127.48 (CH), 127.04 (C), 126.04 (C), 125.93 (C), 125.92 (C), 125.88 (C), 125.87 (C), 125.83 (C), 125.79 (C), 125.73 (C), 125.57 (C), 124.90 (C), 123.38 (C), 118.84 (C), 116.72 (CH), 115.40 (CH), 109.30 (C), 93.87 (C), 92.98 (C), 92.84 (C), 92.79 (C), 92.67 (C), 92.62 (C), 92.59 (C), 92.56 (C), 92.45 (C), 92.37 (C), 91.53 (C), 88.49 (C), 74.86 (CH), 66.80 (CH_2), 26.88 (CH_3). **HRMS (ESI):** *m*/*z* $[M+Na]^+$ calcd for $C_{117}H_{68}O_4$: 1559.5015; found: 1559.5010.

*Synthesis of the intermediate **19***

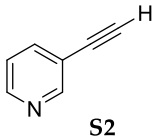
Compound S1



S1

Compound **S1** was prepared from 3-bromopyridine (1.20 g, 7.60 mmol) and (triisopropylsilyl)acetylene (2.10 mL, 15.0 mmol) according to previously described *GP2* for 3h to give **S1** (1.33 g, 100%) as a colourless oil. The product was characterised and showed NMR spectra identical to reported data.[5] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 – 8.66 (m, 1H), 8.52 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.75 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.29 – 7.21 (m, 1H), 0.26 (s, 9H).

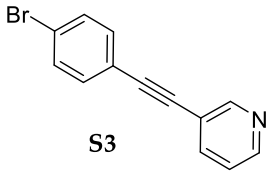
Compound S2



S2

Due to the volatility of **S2**, the TMS protecting group was not removed following the previously described *GP3*. Instead, to a solution of **S1** (1.33 g, 7.59 mmol) in THF (8 ml) with a 4-5 drops of water, Bu_4NF (479 mg, 1.52 mmol) was added, and the mixture was stirred at room temperature until complete consumption of the starting material (TLC, 1 h). The solution was then diluted with diethyl ether, washed with saturated aq NH_4Cl solution, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, Hexane/CH_2Cl_2, 8:2) to give **S2** (626 mg, 80%) as a colourless oil. The product was characterised and showed NMR spectra identical to reported data.[6]

Compound S3

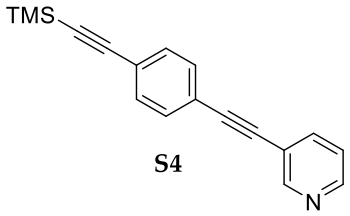


S3

S3 was prepared from **S2** (626 mg, 6.07 mmol) and *p*-bromoiodobenzene (1.15 g, 4.05 mmol) according to previously described *GP1* for 24h to give **S3** (961 mg, 92%) as a white solid. The product

was characterised and showed NMR spectra identical to reported data.[7] **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.75 (s, 1H), 8.54 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.77 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.26 (dd, *J* = 7.8, 5.0 Hz, 1H).

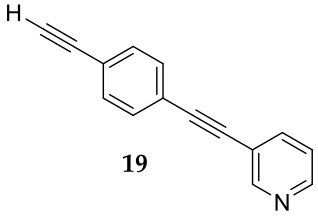
Compound S4



S4

Compound **S4** was prepared from **S3** (961 mg, 3.72 mmol) and (triisopropylsilyl)acetylene (1.03 mL, 7.45 mmol) according to previously described *GP2* for 24h to give **S4** (1.03 g, 100%) as a yellowish white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.76 (s, 1H), 8.55 (d, *J* = 5.1 Hz, 1H), 7.79 (dt, *J* = 7.9, 1.9 Hz, 1H), 7.48 – 7.44 (m, 4H), 7.28 (dd, *J* = 7.9, 5.1 Hz, 1H), 0.25 (s, 9H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.4(CH), 148.9(CH), 138.5(CH), 132.1(CH), 131.6(CH), 123.7(C), 123.2(CH), 122.6(C), 120.4(C), 104.6(C), 96.8(C), 92.4(C), 87.9(C), 0.0(CH_3). **HRMS (ESI):** *m*/*z* $[M+H]^+$ calcd for $C_{18}H_{18}NSi$: 276.1209; found: 276.1202.

Compound 19

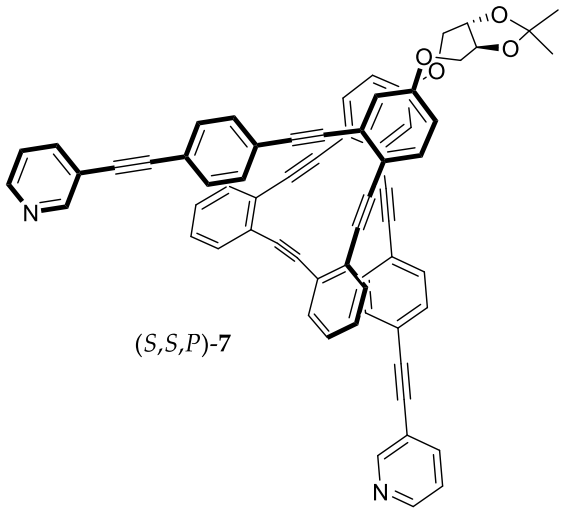


19

19 was prepared from **S4** (1.03 g, 3.72 mmol) according to previously described *GP3* for 2h to give **19** (757 mg, 100%) as a yellowish white solid. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.77 (s, 1H), 8.56 (d, *J* = 5.1 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.49 – 7.48 (m, 4H), 7.27 (t, *J* = 6.7 Hz, 1H), 3.21 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 152.3(CH), 148.9(CH), 138.5(CH), 132.2(CH), 131.6(CH), 123.1(C), 123.0(CH), 122.5(C), 120.2(C), 92.1(C), 87.9(C), 83.2(C), 79.4(C). **HRMS (ESI):** *m*/*z* $[M+H]^+$ calcd for $C_{15}H_{10}N$: 204.0813; found: 204.0806.

Synthesis of ligand (S,S,P)-7

Compound (*S,S,P*)-7



(*S,S,P*)-**7**

Was prepared from (*S,S,P*)-**1** (200 mg, 0.29 mmol) and **19** (176 mg, 0.86 mmol) according to previously described *GP2* for 24h to give (*S,S,P*)-**7** (221 mg, 81%) as a yellow solid. It was characterised both in CD_2Cl_2 and *d*-DMSO.

CD_2Cl_2

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.74 (s, 2H), 8.54 (bsignal, 2H), 7.80 (dt, *J* = 7.8, 1.7 Hz, 2H), 7.63 (dd, *J* = 7.6, 1.4 Hz, 2H), 7.48 (dt, *J* = 7.6, 0.7 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 4H), 7.37 – 7.26 (m, 8H), 7.21 (d, *J* = 8.1 Hz, 4H), 6.76 (d, *J* = 2.6 Hz, 2H), 6.51 (dd, *J* = 8.6, 2.7 Hz, 2H), 4.42 – 4.36 (m, 4H), 4.35 – 4.29 (m, 2H), 1.50 (s, 6H). **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 158.0(C), 152.7(CH), 149.3(CH), 138.8(CH), 134.2(CH), 133.7(CH), 132.4(CH), 131.8(CH), 128.7(CH), 128.4(CH), 127.1(C), 125.7(C), 125.2(C), 124.2(C), 123.6(CH), 122.7(C), 119.5(C), 117.7(CH), 115.3(CH), 109.9(C), 93.7(C), 93.2(C), 93.1(C), 92.7(C), 91.7(C), 90.9(C), 88.2(C), 75.3(CH), 67.5(CH_2), 27.2(CH_3). **HRMS (ESI):** *m/z* $[M+H]^+$ calcd for $C_{67}H_{43}N_2O_4$: 939.3223; found: 939.3252.

DMSO-d_6

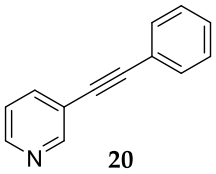
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.71 (s, 2H), 8.56 (d, *J* = 4.9 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.71 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.49 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.46 – 7.36 (m, 10H), 7.29 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 4H), 6.82 (d, *J* = 1.2 Hz, 2H), 6.67 (dd, *J* = 8.7, 1.2 Hz, 2H), 4.44 – 4.26 (m, 6H), 1.42 (s, 6H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 157.4(C), 151.6(CH), 149.1(CH), 138.5(CH),

133.8(CH), 133.6(CH), 133.1(CH), 131.6(CH), 131.1(CH), 128.8(CH), 128.4(CH), 125.6(C), 124.3(C), 123.7(C), 123.6(CH), 122.9(C), 121.5(C), 119.2(C), 117.8(C), 117.4(CH), 115.2(CH), 108.6(C), 92.7(C), 92.6(C), 92.4(C), 91.8(C), 90.7(C), 90.3(C), 87.9(C), 74.1(CH), 66.6(CH_2), 26.8(CH_3).

*Synthesis of the model compound **20***

In order to study the metal-pyridine coordination of our final compound **(*S*,*S*)-7** and compare its behaviour to a similar simpler structure, the model compound **20** was synthesised.

Compound 20



20

Was prepared from 3-bromopyridine (0.12 mL, 1.26 mmol) and phenylacetylene (0.28 mL, 2.53 mmol) according to previously described *GP2* for 24h to give **20** (225 mg, 100%) as a yellow solid. It was characterised both in CD_2Cl_2 and *d*-DMSO.

CD_2Cl_2

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.75 (s, 1H), 8.53 (d, *J* = 4.4 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.42 – 7.36 (m, 3H), 7.30 (dd, *J* = 7.9, 4.9 Hz, 1H). **^{13}C NMR (101 MHz, CD_2Cl_2)** δ 152.8(CH), 149.3(CH), 138.8(CH), 132.2(CH), 129.4(CH), 129.1(CH), 123.6(CH), 123.2(C), 120.9(C), 92.9(C), 86.5(C). **HRMS (GC-EI+):** *m*/*z* $[M]^+$ calcd for $C_{13}H_9N$: 179.0735; found: 179.0741.

DMSO-d_6

^{1}H NMR (500 MHz, DMSO-d_6) δ 8.76 (d, *J* = 2.2 Hz, 1H), 8.59 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.98 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.60 – 7.57 (m, 2H), 7.49 – 7.43 (m, 4H). **^{13}C NMR (126 MHz, DMSO-d_6)** δ 151.6(CH), 149.0(CH), 138.6(CH), 131.5(CH), 129.3(CH), 128.9(CH), 123.7(CH), 121.7(C), 119.4(C), 92.3(C), 86.1(C).

*Synthesis of (S,S,P)-**1-7**:Ag(I) complexes*

The corresponding compounds (*S,S,P*)-**1-7** (0.024 mmol, 1 eq.) were dissolved in a 9:1 mixture of CD_2Cl_2: Acetone-d_6 (0.5 mL). On the other hand, a solution of $AgBF_4$ (0.120 mmol, 5 eq.) in 9:1 CD_2Cl_2: Acetone-d_6 (0.5 mL) was prepared. Finally, both solutions were mixed and the corresponding ^1H NMR spectra recorded (see Section 3).

Complex (*S,S,P*)-1:Ag(I)

^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) δ 7.98 – 7.88 (m, 2H), 7.87 – 7.80 (m, 2H), 7.68 – 7.55 (m, 6H), 6.91 – 6.81 (m, 4H), 4.43 – 4.26 (m, 6H), 1.47 (s, 6H). **^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6)** δ 161.1(C), 136.1(CH), 134.8(CH), 134.2(CH), 131.4(CH), 131.3(CH), 127.4(C), 125.0(C), 123.2(C), 120.1(CH), 114.5(CH), 113.5(C), 110.5(C), 94.2(C), 92.9(C), 89.1(C), 75.1(CH), 68.4(CH_2), 27.1(CH_3).

Complex (*S,S,P*)-2:Ag(I)

^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) δ 7.76 (d, *J* = 8.7 Hz, 2H), 7.68 – 7.65 (m, 2H), 7.49 – 7.45 (m, 2H), 7.44 – 7.37 (m, 8H), 7.08 (dd, *J* = 8.8, 2.6 Hz, 2H), 7.04 – 6.98 (m, 6H), 6.61 (d, *J* = 2.6 Hz, 2H), 4.45 – 4.40 (m, 4H), 4.38 – 4.34 (m, 2H), 1.48 (s, 6H). **^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6)** δ 160.44(C), 134.77(CH), 134.24(CH), 133.92(CH), 132.48(CH), 131.05(CH), 130.62(CH), 130.56(CH), 128.92(CH), 127.15(C), 124.33(C), 122.27(C), 120.37(C), 115.03(C), 110.21(C), 98.33(C), 93.99(C), 91.59(C), 90.42(C), 87.51(C), 75.37(CH), 68.14(CH_2), 27.07(CH_3).

Complex (*S,S,P*)-3:Ag(I)

^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) δ 7.61 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.1 Hz, 4H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.11 (m, 2H), 7.11 (d, *J* = 7.4 Hz, 4H), 7.07 (d, *J* = 8.1 Hz, 4H), 7.04 (d, *J* = 7.6 Hz, 2H), 7.03 – 6.98 (m, 4H), 6.87 (dd, *J* = 8.7, 2.3 Hz, 2H), 6.63 (d, *J* = 2.6 Hz, 2H), 4.39 – 4.32 (m, 6H), 1.51 (s, 6H). **^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6)** δ 159.99 (C), 135.49 (CH), 133.46 (CH), 133.32 (CH), 132.87 (CH), 132.14 (CH), 132.07 (CH), 130.36 (CH), 130.31 (CH), 129.99 (CH), 129.61 (CH), 128.89 (CH), 128.80 (CH), 126.63 (C), 126.01 (C), 123.94 (C), 123.20 (C), 122.59 (C), 122.28 (C), 115.30 (C), 96.28 (C), 96.04 (C), 93.53 (C), 92.33 (C), 91.63 (C), 90.80 (C), 88.18 (C), 75.19 (CH), 68.02 (CH_2), 27.09 (CH_3).

Complex (*S*,*S*,*P*)-4:Ag(I)

^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 4H), 7.31 – 7.23 (m, 6H), 7.20 – 7.07 (m, 22H), 6.99 (d, *J* = 7.7 Hz, 2H), 6.83 (dd, *J* = 8.8, 2.7 Hz, 2H), 6.42 (bs, 2H), 4.36 – 4.26 (m, 6H), 1.50 (s, 6H). **^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6)** δ 159.7(C), 135.5(CH), 133.6(CH), 133.5(CH), 132.9(CH), 132.8(CH), 132.4(CH), 132.3(CH), 130.7(CH), 130.2(CH), 129.9(CH), 129.3(CH), 128.9(CH), 125.5(C), 124.8(C), 124.6(C), 123.7(C), 123.4(C), 123.1(C), 122.5(C), 94.4(C), 94.2(C), 93.8(C), 92.4(C), 92.1(C), 92.0(C), 87.9(C), 75.0(CH), 67.9(CH_2), 27.1(CH_3).

Complex (*S*,*S*,*P*)-5:Ag(I)

^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.35 (m, 7H), 7.28 – 7.18 (m, 7H), 7.18 – 7.08 (m, 13H), 7.07 – 7.03 (m, 3H), 6.99 (td, *J* = 7.6, 1.2 Hz, 2H), 6.96 – 6.87 (m, 8H), 6.85 – 6.79 (m, 4H), 6.50 (s, 2H), 4.46 – 4.32 (m, 6H), 1.50 (s, 6H). **^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6)** δ 159.71 (C), 135.38 (CH), 133.77 (CH), 133.68 (CH), 133.51 (CH), 133.10 (CH), 133.01 (CH), 132.97 (CH), 132.83 (CH), 132.30 (CH), 132.26 (CH), 132.16 (CH), 131.02 (CH), 130.83 (CH), 130.75 (CH), 130.65 (CH), 130.61 (CH), 130.54 (CH), 129.90 (CH), 129.46 (CH), 128.67 (CH), 125.60 (C), 123.97 (C), 123.87 (C), 123.82 (C), 123.01 (C), 122.84 (C), 122.62 (C), 122.54 (C), 122.46 (C), 121.56 (CH), 121.29 (C), 115.67 (C), 115.04 (CH), 95.38 (C), 95.29 (C), 93.93 (C), 93.52 (C), 93.22 (C), 93.13 (C), 92.67 (C), 92.55 (C), 92.12 (C), 88.02 (C), 74.78 (CH), 67.81 (CH_2), 31.03 (CH_3).

Complex (*S*,*S*,*P*)-6:Ag(I)

^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:Acetone-d_6) δ 7.42 (t, *J* = 7.5 Hz, 4H), 7.32 – 7.19 (m, 10H), 7.17 (dt, *J* = 6.9, 1.4 Hz, 5H), 7.17 – 7.10 (m, 3H), 7.09 (d, *J* = 7.4 Hz, 2H), 7.08 – 6.88 (m, 28H), 6.83 (dd, *J* = 8.8, 2.6 Hz, 2H), 6.74 (d, *J* = 7.7 Hz, 1H), 6.24 (bsignal, 1H), 4.35 – 4.17 (m, 6H), 1.52 (s, 6H). **^{13}C NMR (101 MHz, 9:1 CD_2Cl_2:Acetone-d_6)** δ 135.49 (CH), 133.85 (CH), 133.42 (CH), 133.27 (CH), 133.17 (CH), 133.09 (CH), 132.93 (CH), 132.60 (CH), 132.53 (CH), 132.30 (CH), 130.83 (CH), 130.80 (CH), 130.70 (CH), 130.62 (CH), 130.58 (CH), 130.53 (CH), 130.31 (CH), 129.89 (CH), 128.89 (CH), 124.17 (C), 124.13 (C), 123.76 (C), 123.05 (C), 122.99 (C), 122.90 (C), 122.74 (C), 122.65 (C), 122.61 (C), 122.37 (C), 121.45 (CH), 115.46 (CH), 115.35 (C), 96.46 (C), 94.01 (C), 93.87 (C), 93.76 (C), 93.70 (C), 93.40 (C), 92.95 (C), 92.66 (C), 92.54 (C), 92.52 (C), 92.49 (C), 92.30 (C), 74.95 (CH), 67.91 (CH_2), 31.09 (CH_3).

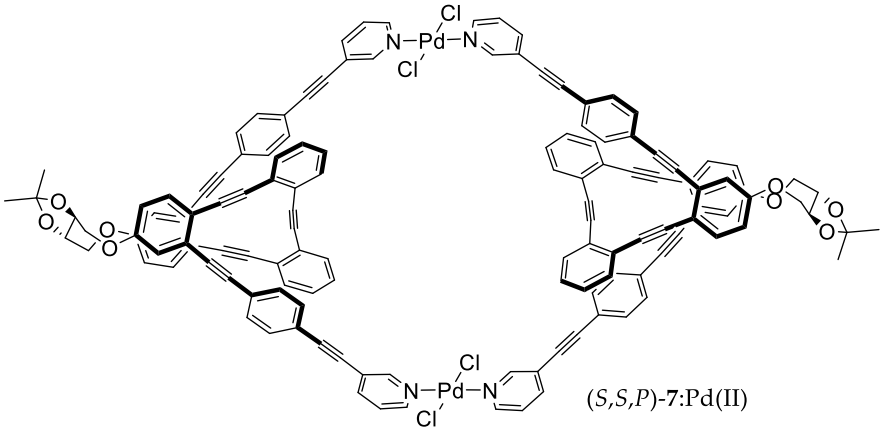
Complex (*S*,*S*,*P*)-7:Ag(I)

^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) δ 8.80 (s, 2H), 8.53 (s, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.36 (m, 4H), 7.34 – 7.29 (m, 4H), 7.26 (d, *J* = 8.0 Hz, 4H), 7.09 (d, *J* = 7.7 Hz, 4H), 6.79 – 6.75 (m, 2H), 6.59 – 6.54 (m, 2H), 4.45 – 4.39 (m, 4H), 4.35 – 4.30 (m, 2H), 1.51 (s, 6H). **^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6)** δ 158.0(C), 154.2(CH), 150.4(CH), 140.4(CH), 134.3(CH), 134.2(CH), 133.9(CH), 132.3(CH), 131.8(CH), 128.9(CH), 128.6(CH), 127.1(C), 125.8(C), 125.1(C), 124.8(CH), 124.4(C), 122.2(C), 122.0(C), 119.4(C), 117.7(CH), 115.2(CH), 109.9(C), 94.5(C), 93.8(C), 93.4(C), 93.2(C), 91.4(C), 91.0(C), 86.8(C), 75.2(CH), 67.5(CH_2), 27.1(CH_3).

*Synthesis of (S,S,P)-**7**:Pd(II) and **20**:Pd(II) complexes*

The corresponding compounds (*S*,*S*,*P*)-**7** and **20** were dissolved in (5 mM and 10 mM respectively) of CD_2Cl_2 (0.5 mL). On the other hand, a solution of $Pd(CH_3CN)_2Cl_2$ in 0.5 mL (5 mM and 10 mM) of CD_2Cl_2 was prepared. Finally, both solutions were mixed and the corresponding ^{1}H NMR spectra recorded. (*S*,*S*,*P*)-**7:**Pd(II) is only partially soluble in CD_2Cl_2, so it was necessary to make the spectroscopical characterization immediately after the synthesis. Both complexes were also characterised in DMSO-d_6.

Complex (*S*,*S*,*P*)-7:Pd(II)



(*S*,*S*,*P*)-**7**:Pd(II)

CD_2Cl_2

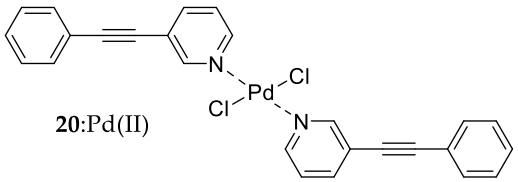
^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.99 (s, 2H), 8.87 (d, *J* = 5.8 Hz, 2H), 7.77 – 7.69 (m, 4H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 4H), 7.09 – 7.03 (m, 6H), 6.76

(d, *J* = 2.7 Hz, 2H), 6.55 (d, *J* = 8.6 Hz, 2H), 4.46 – 4.37 (m, 4H), 4.35 – 4.29 (m, 2H), 1.51 (s, 6H). **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 158.0(C), 156.0(CH), 152.9(CH), 141.0(CH), 134.4(CH), 134.2(CH), 134.0(CH), 132.3(CH), 131.8(CH), 128.9(CH), 128.7(CH), 127.2(C), 125.8(C), 125.2(C), 124.6(CH), 124.3(C), 122.1(C), 121.7(C), 119.5(C), 117.1(CH), 115.1(CH), 110.0(C), 95.1(C), 93.9(C), 93.4(C), 93.3(C), 91.4(C), 91.1(C), 85.8(C), 75.3(CH), 67.5(CH_2), 27.2(CH_3). **HRMS (MALDI):** *m*/*z* [M-Cl]$^+$ calcd for $C_{134}H_{84}Cl_3N_4O_8Pd_2$: 2197.3457; found: 2197.3428.

DMSO-d$_6$

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.93 (s, 2H), 8.79 (d, *J* = 5.7 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 7.4 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.68 – 7.63 (m, 2H), 7.57 (t, *J* = 7.2 Hz, 3H), 7.50 (d, *J* = 7.3 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.42 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 4H), 6.84 (s, 3H), 6.75 – 6.69 (m, 1H), 4.40 (s, 2H), 4.38 – 4.33 (m, 4H), 1.44 (s, 6H).

Complex 20:Pd(II)



20:Pd(II)

CD_2Cl_2

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.98 (s, 1H), 8.78 (d, *J* = 5.8 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.44 – 7.40 (m, 3H), 7.37 (dd, *J* = 8.0, 5.8 Hz, 1H). **^{13}C NMR (126 MHz, CD_2Cl_2)** δ 155.9(CH), 152.6(CH), 141.5(CH), 132.4(CH), 130.0(CH), 129.2(CH), 125.0(CH), 122.7(C), 122.4(C), 95.2(C), 84.1(C). **LRMS (MALDI):** *m*/*z* [M-Cl]$^+$ calcd for $C_{26}H_{18}ClN_2Pd$: 501.0; found: 501.0.

DMSO-d$_6$

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.99 (d, *J* = 1.9 Hz, 1H), 8.78 (dd, *J* = 5.9, 1.4 Hz, 1H), 8.20 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.67 – 7.60 (m, 2H), 7.51 – 7.44 (m, 4H). **^{13}C NMR (126 MHz, DMSO)** δ 154.5(CH), 152.5(CH), 141.5(CH), 131.7(CH), 129.9(CH), 129.0(CH), 125.5(CH), 121.0(C), 118.1(C), 94.1(C), 83.8(C).

2. NMR SPECTRA OF NEW COMPOUNDS

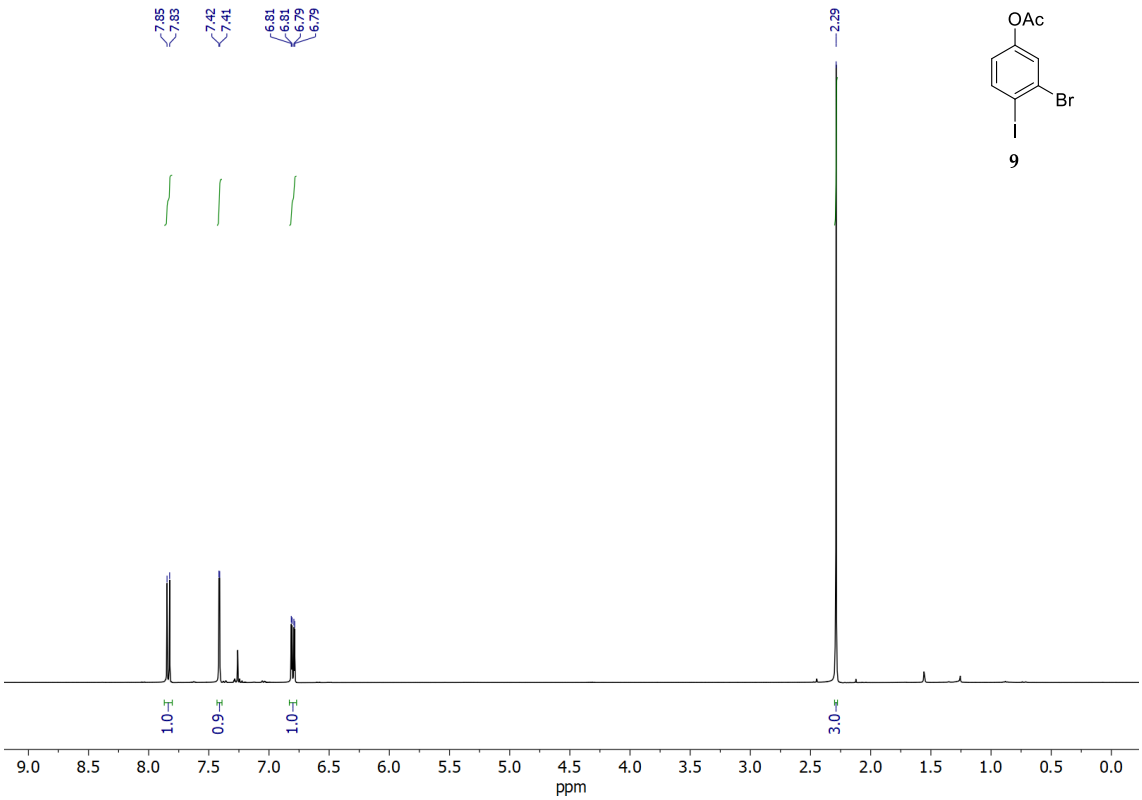


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **9**.

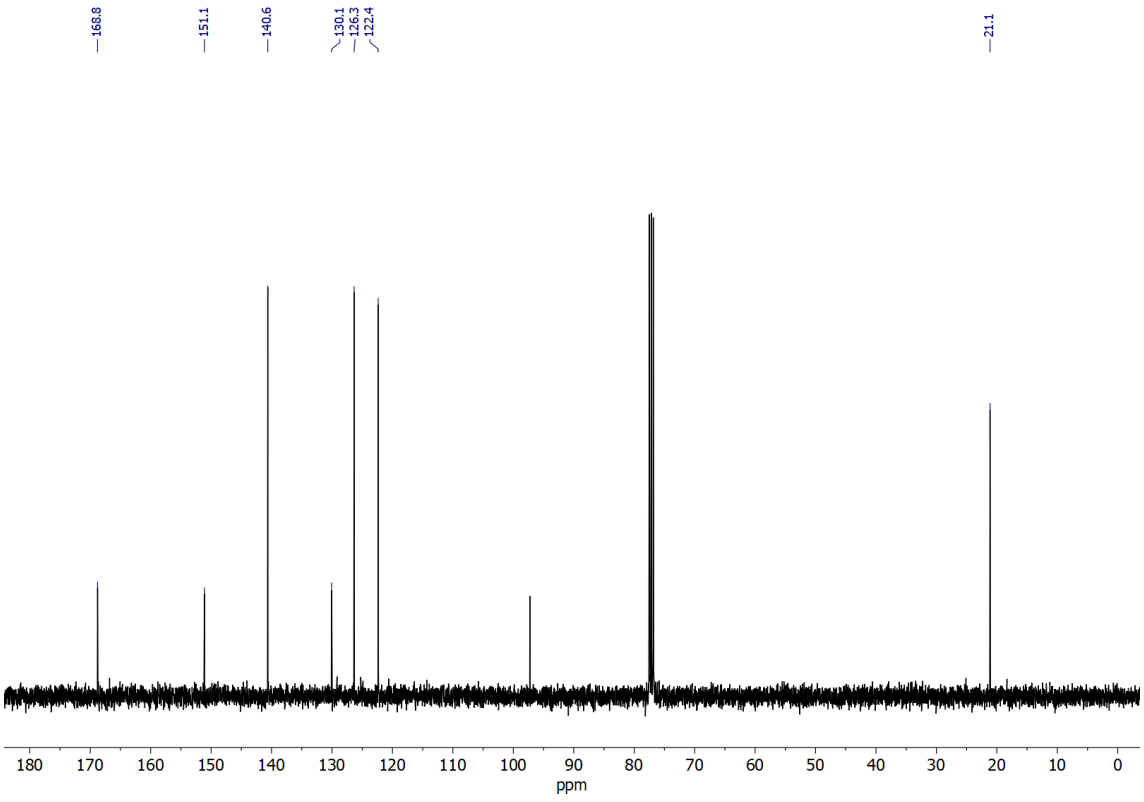


Figure S2. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **9**.

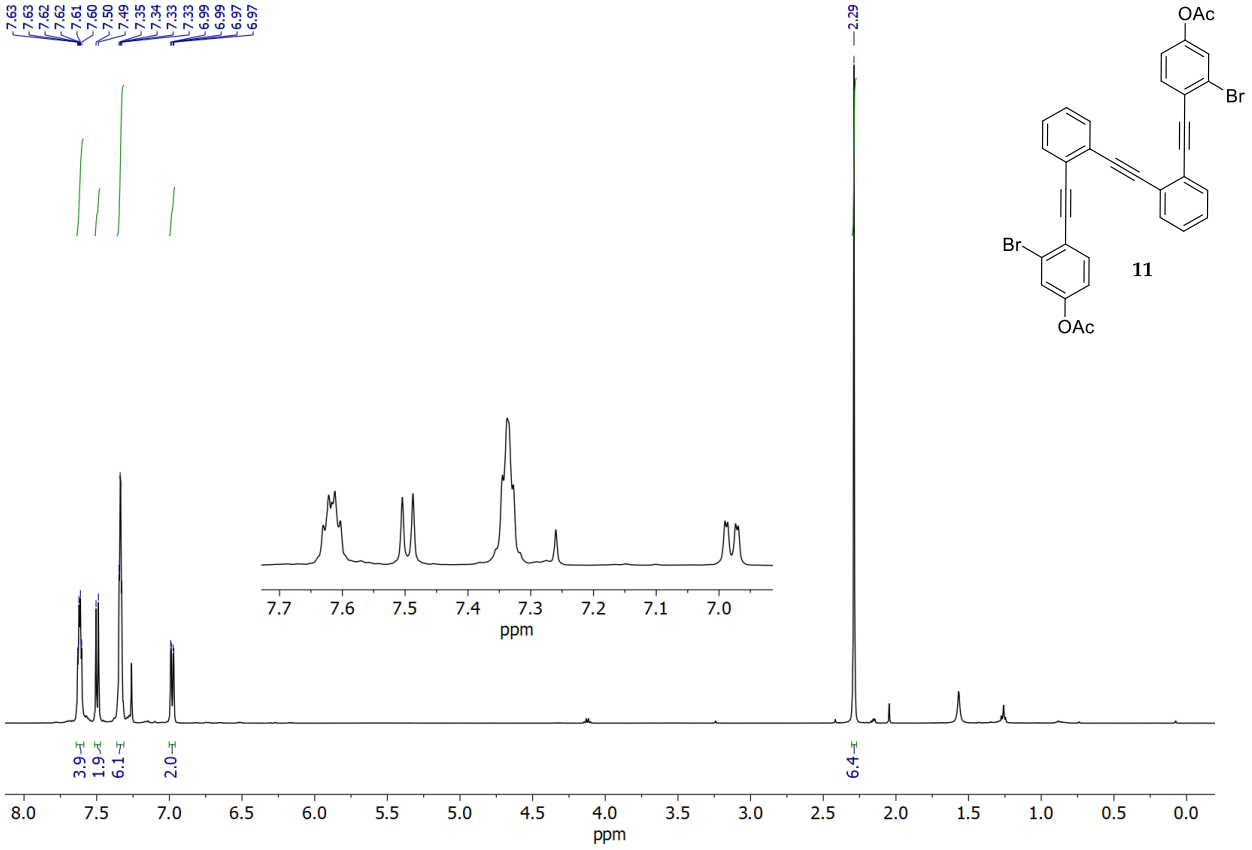


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**.

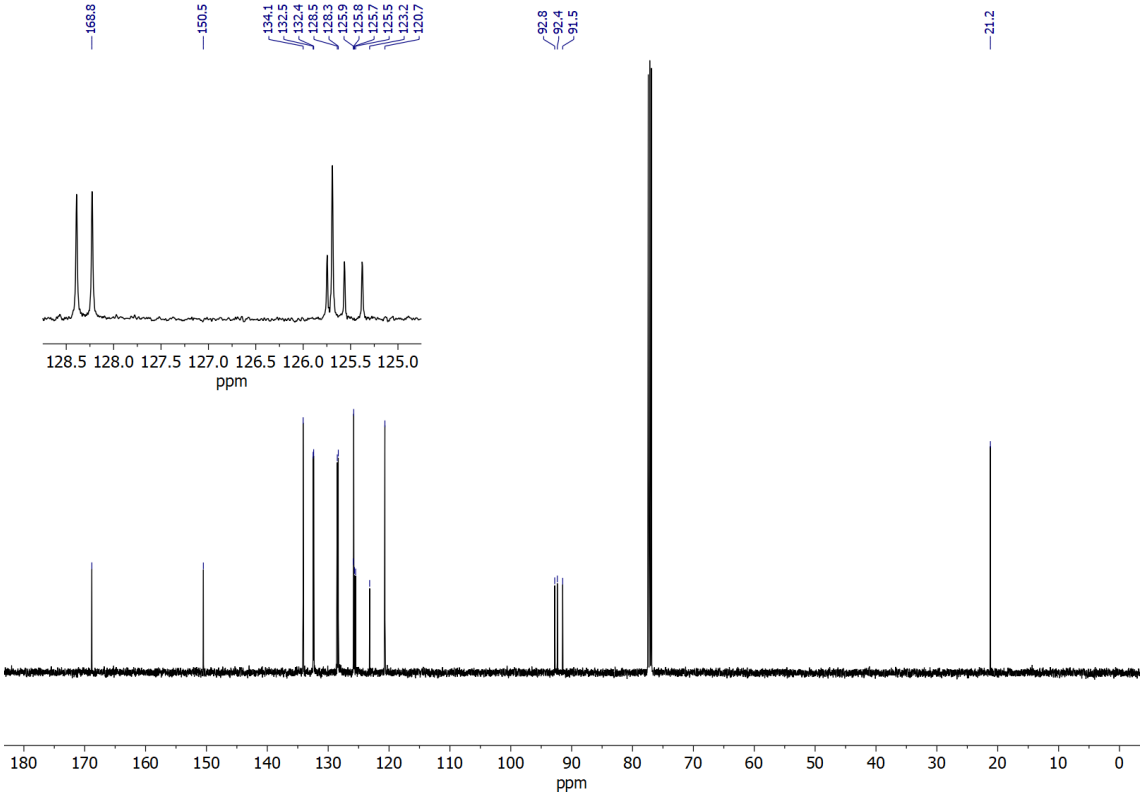


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound **11**.

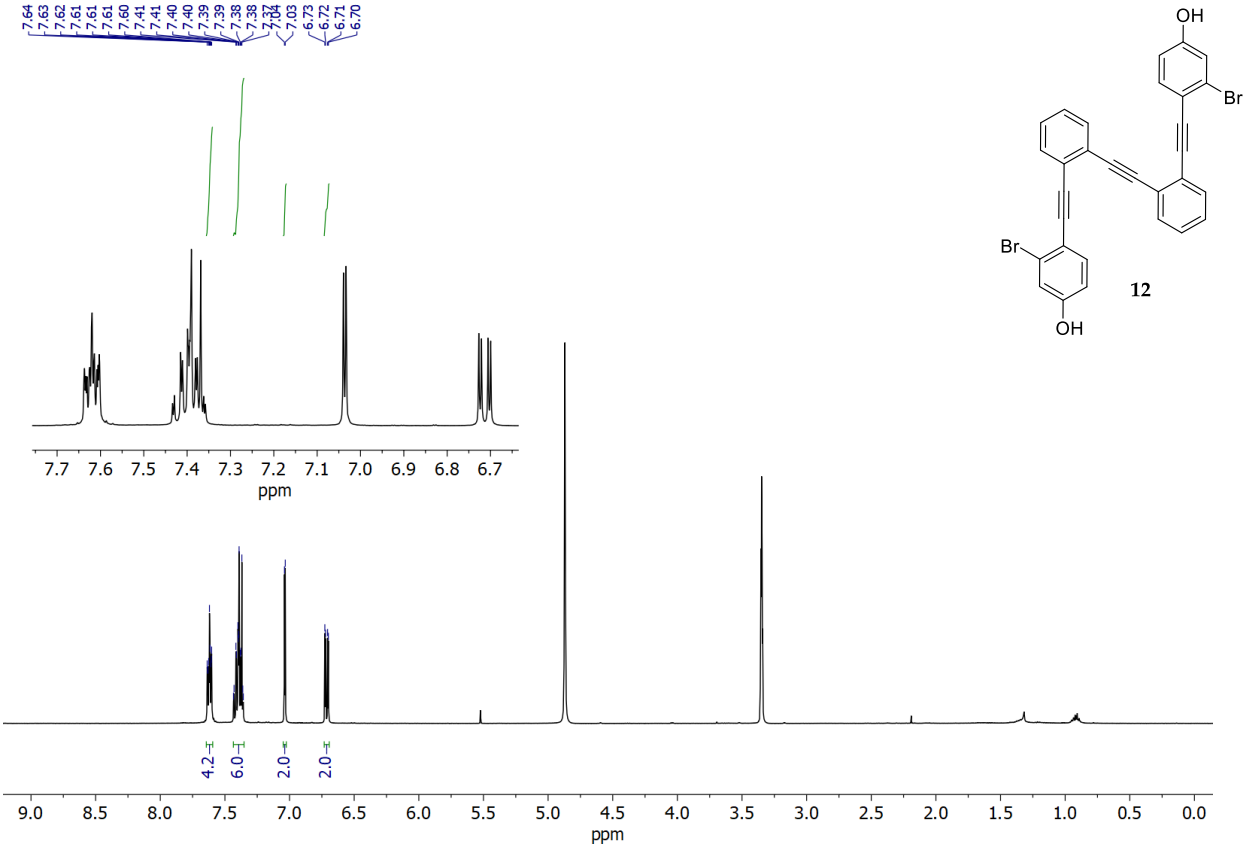


Figure S5. ^{1}H NMR (400 MHz, Methanol-d_4) spectrum of compound **12**.

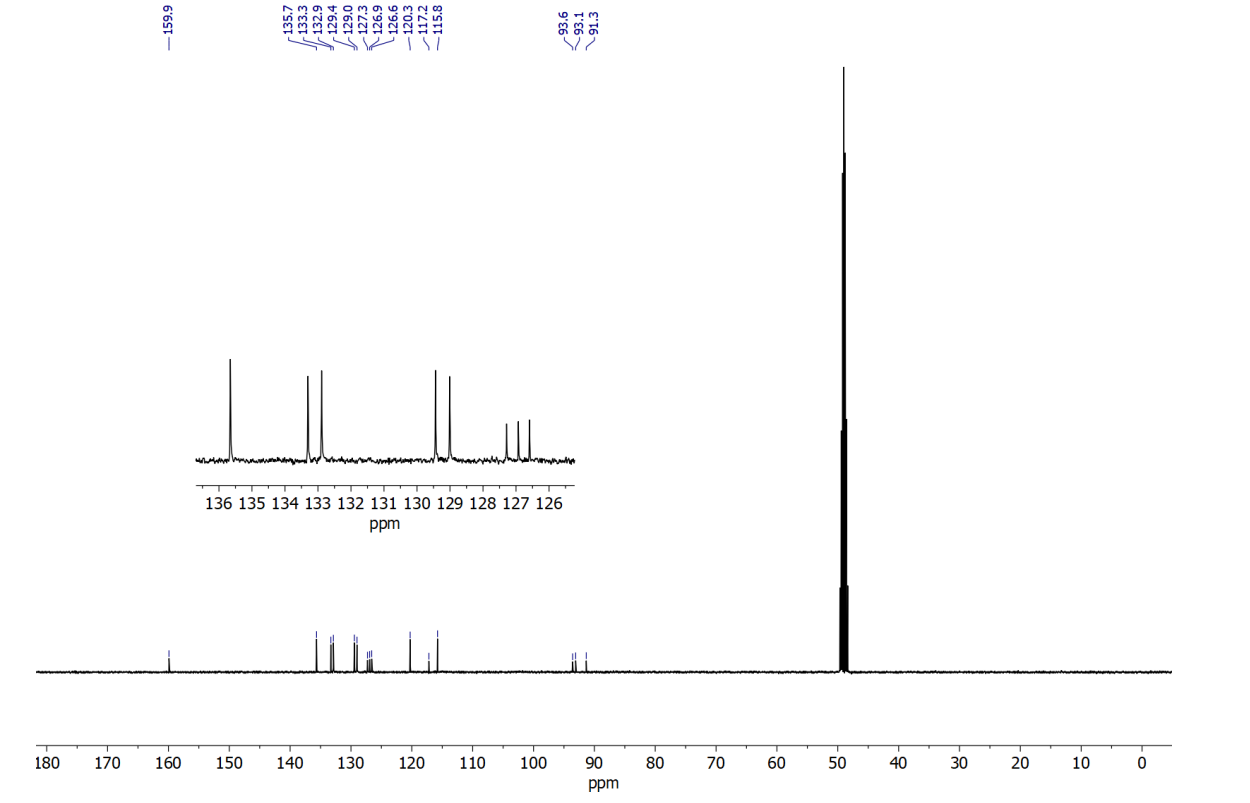


Figure S6. ^{13}C NMR (101 MHz, MeOD) spectrum of compound **12**.

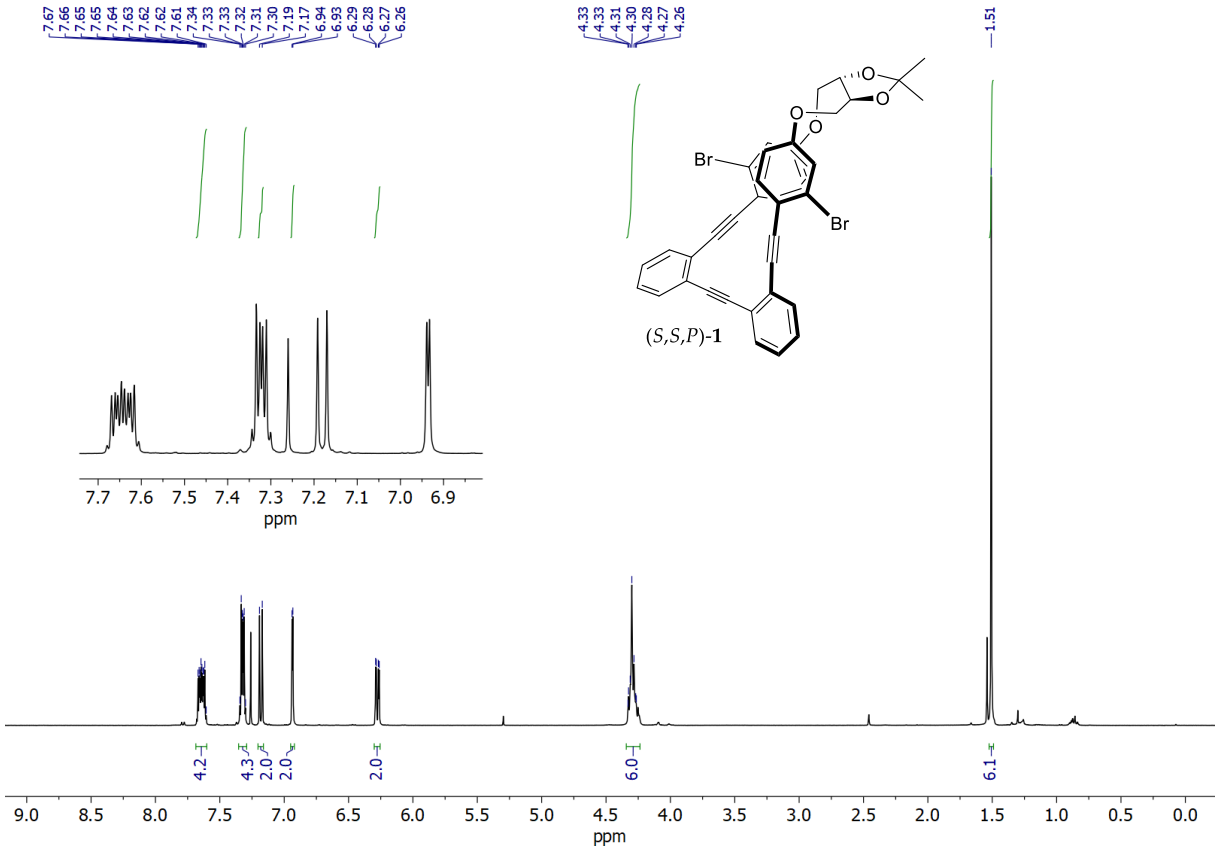


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**1**.

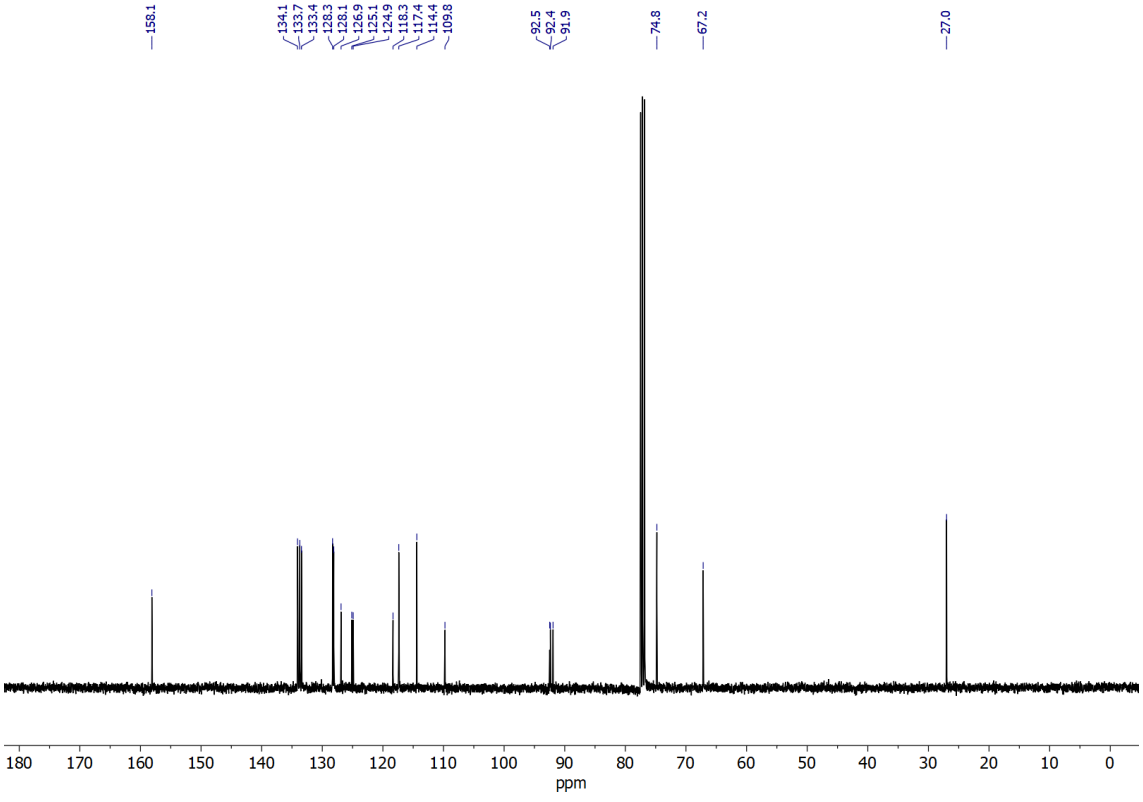


Figure S8. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**1**.

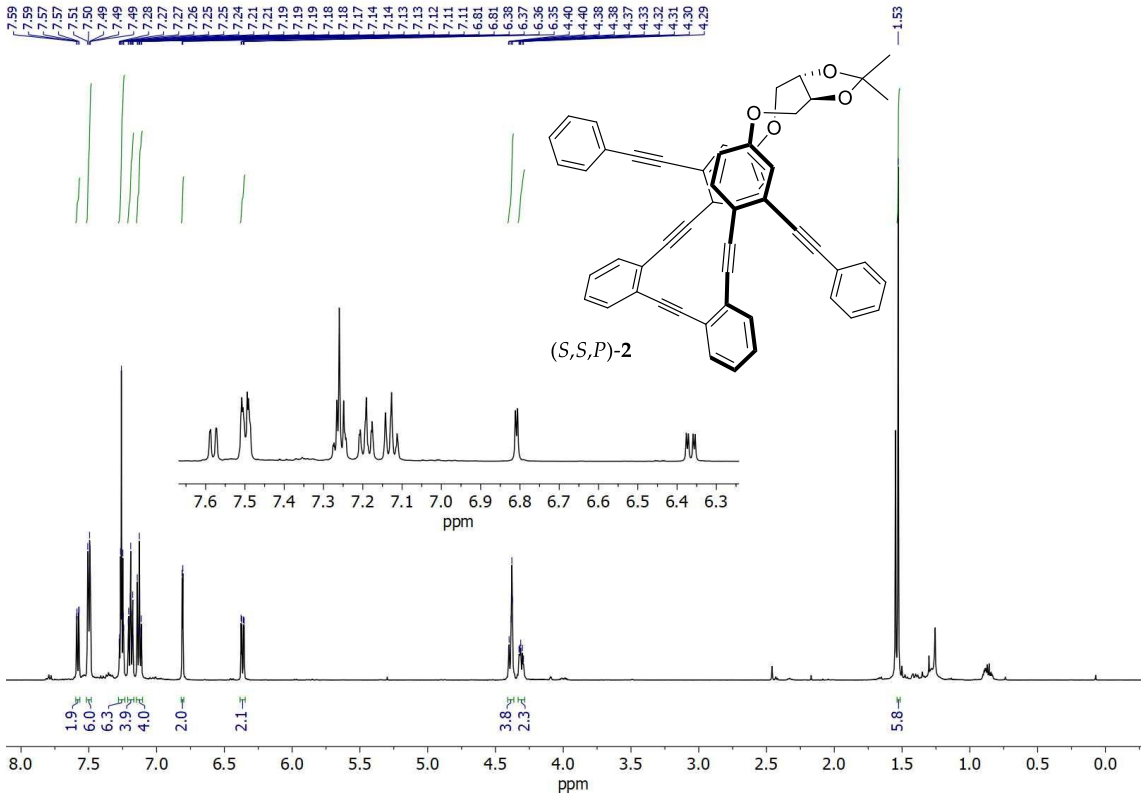


Figure S9. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**2**.

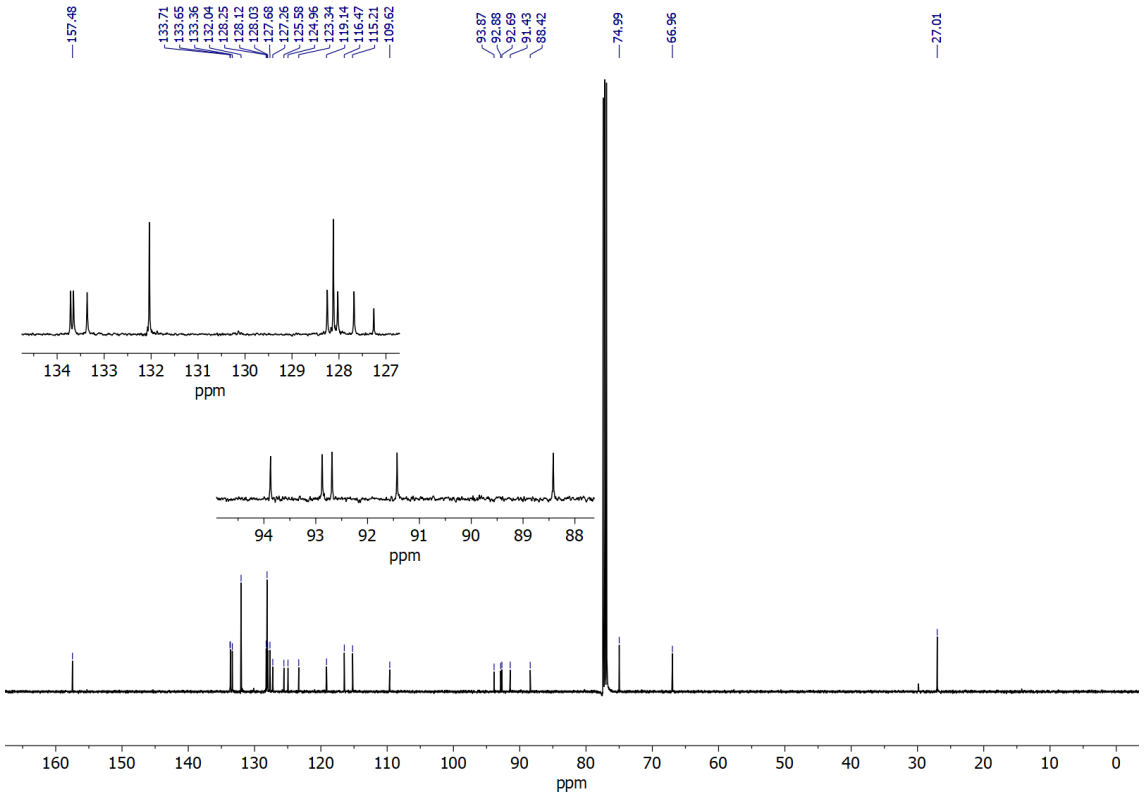


Figure S10. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**2**.

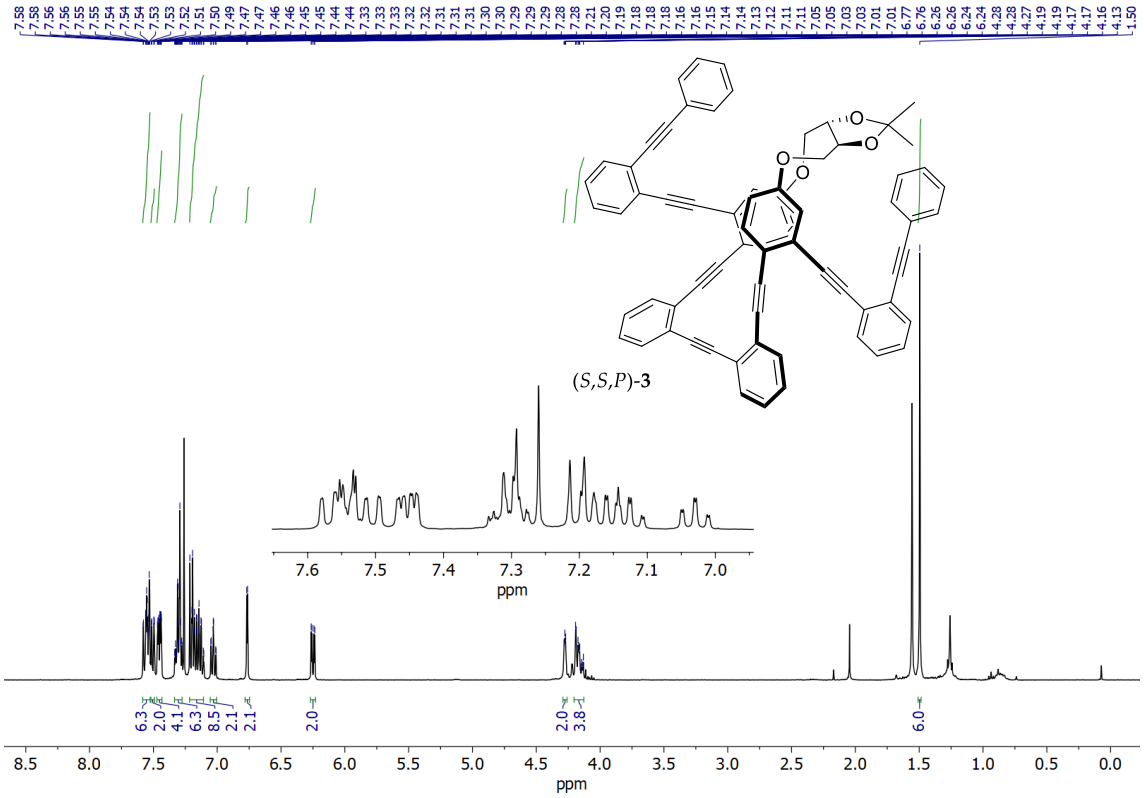


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**3**.

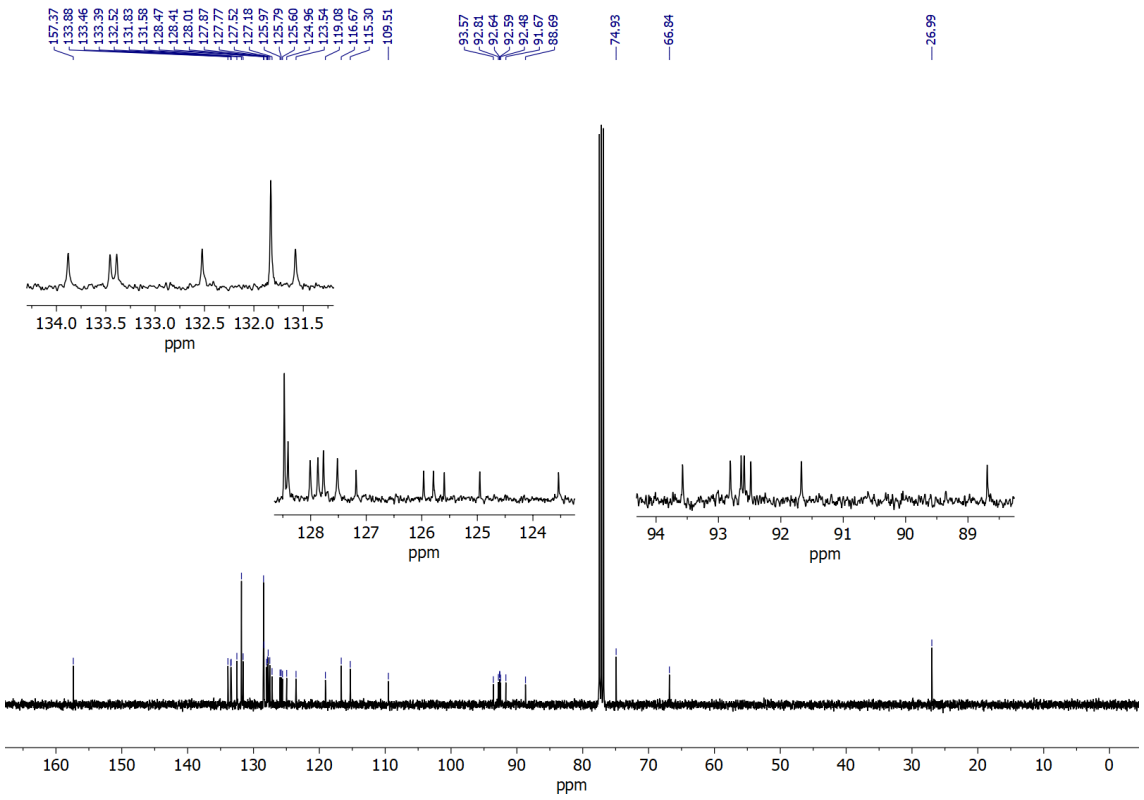


Figure S12. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**3**.

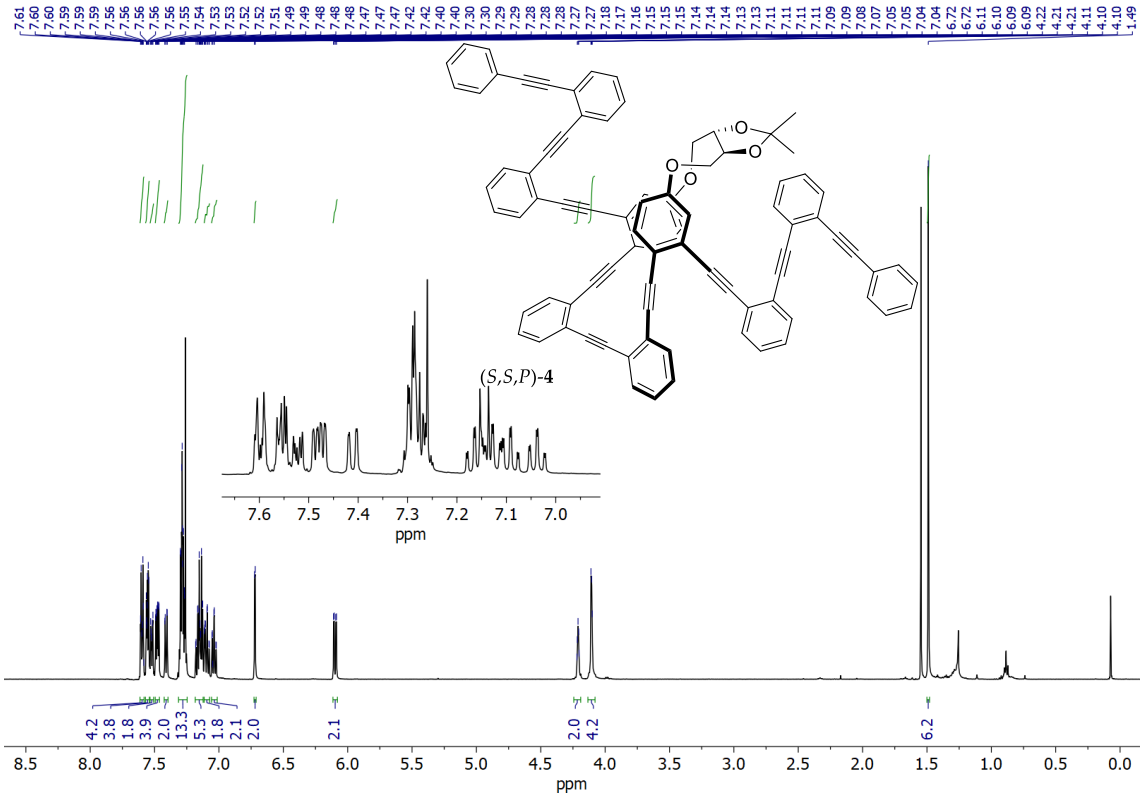


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**4**.

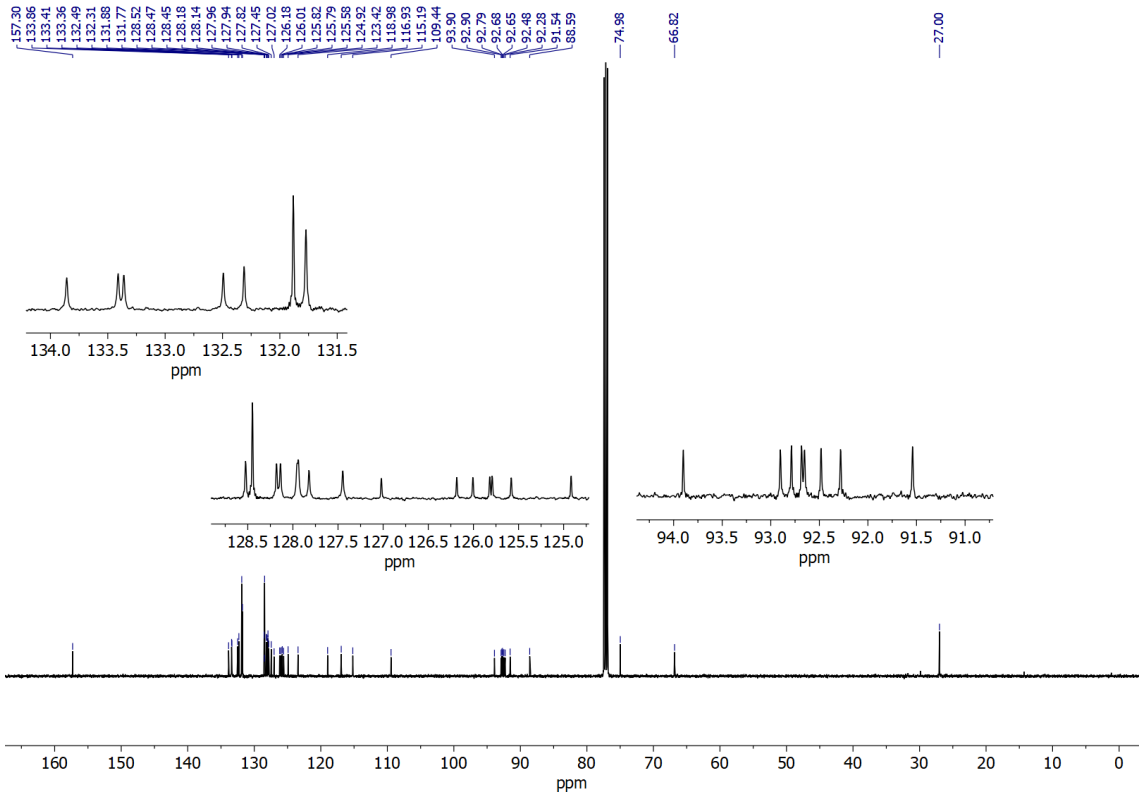


Figure S14. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**4**.

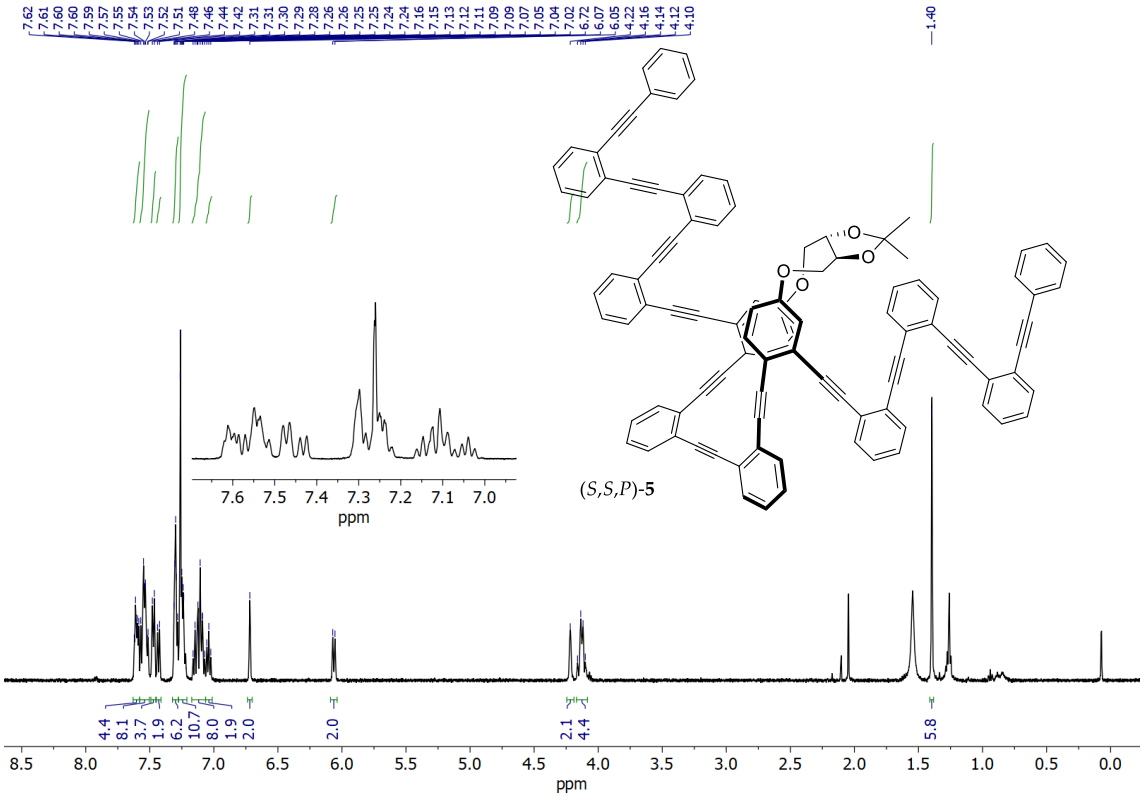


Figure S15. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**5**.

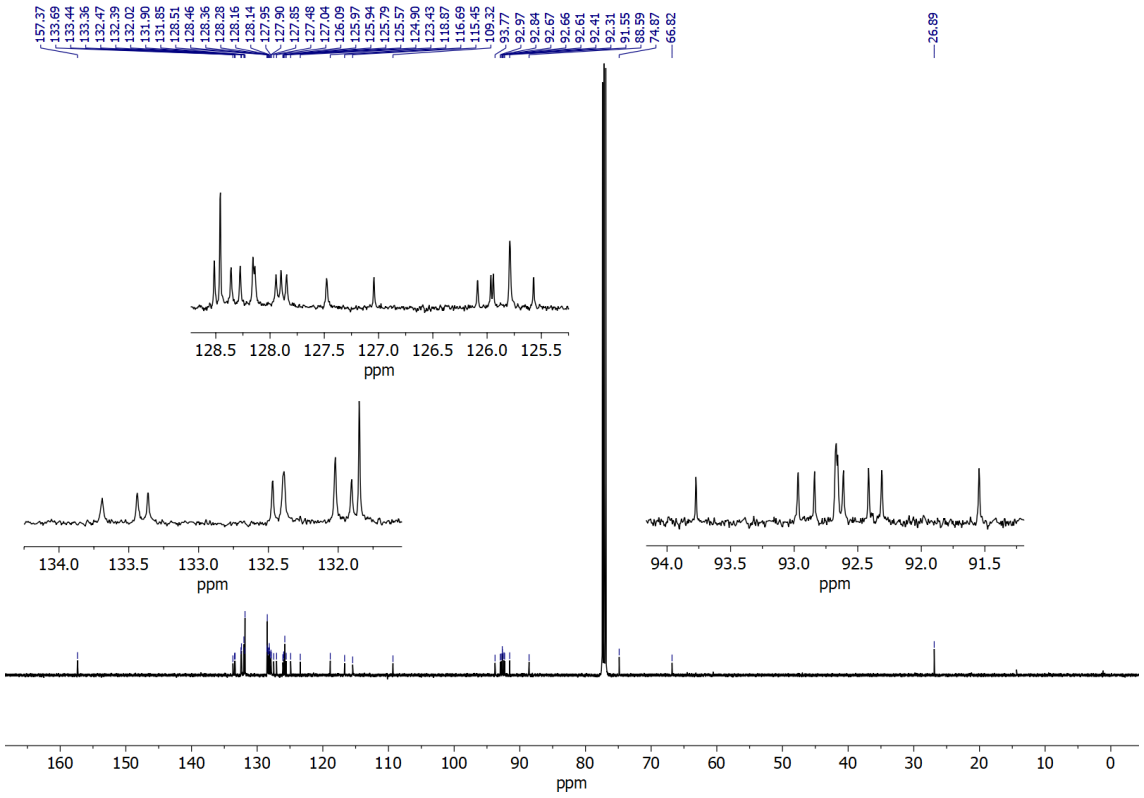


Figure S16. ^{13}C NMR (126 MHz, $CDCl_3$**)** spectrum of compound (*S*,*S*,*P*)-**5**.

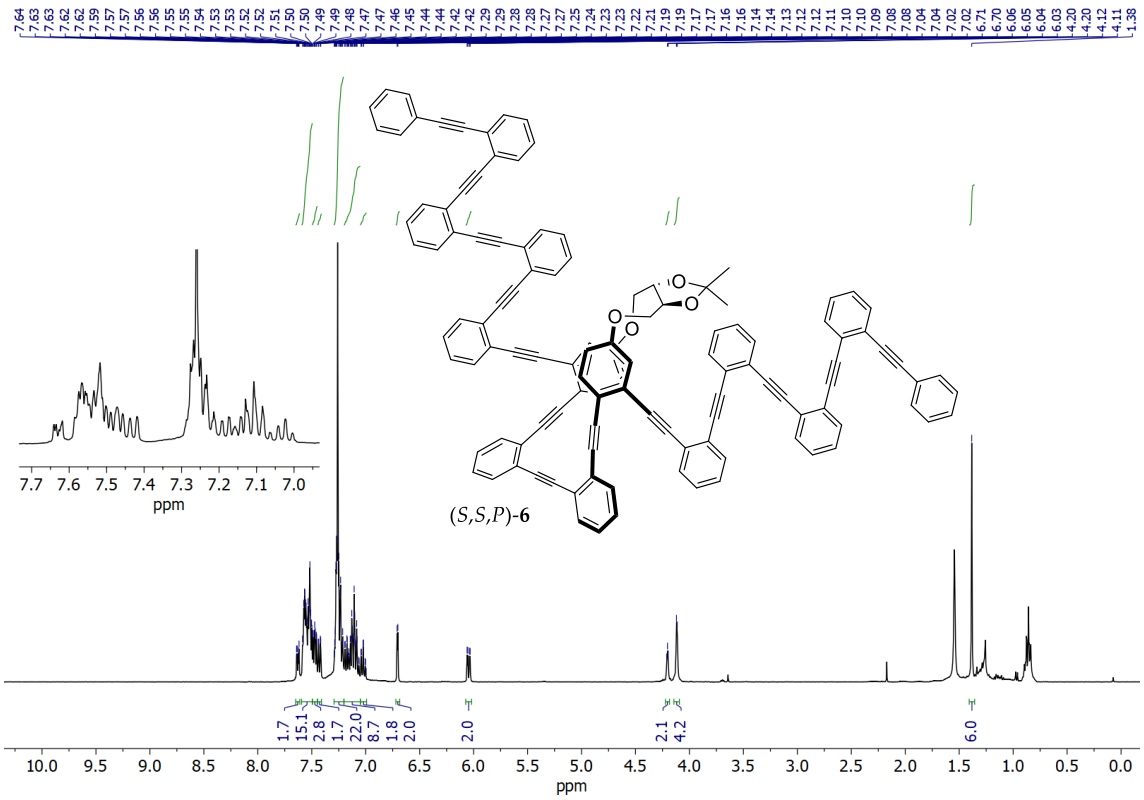


Figure S17. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**6**.

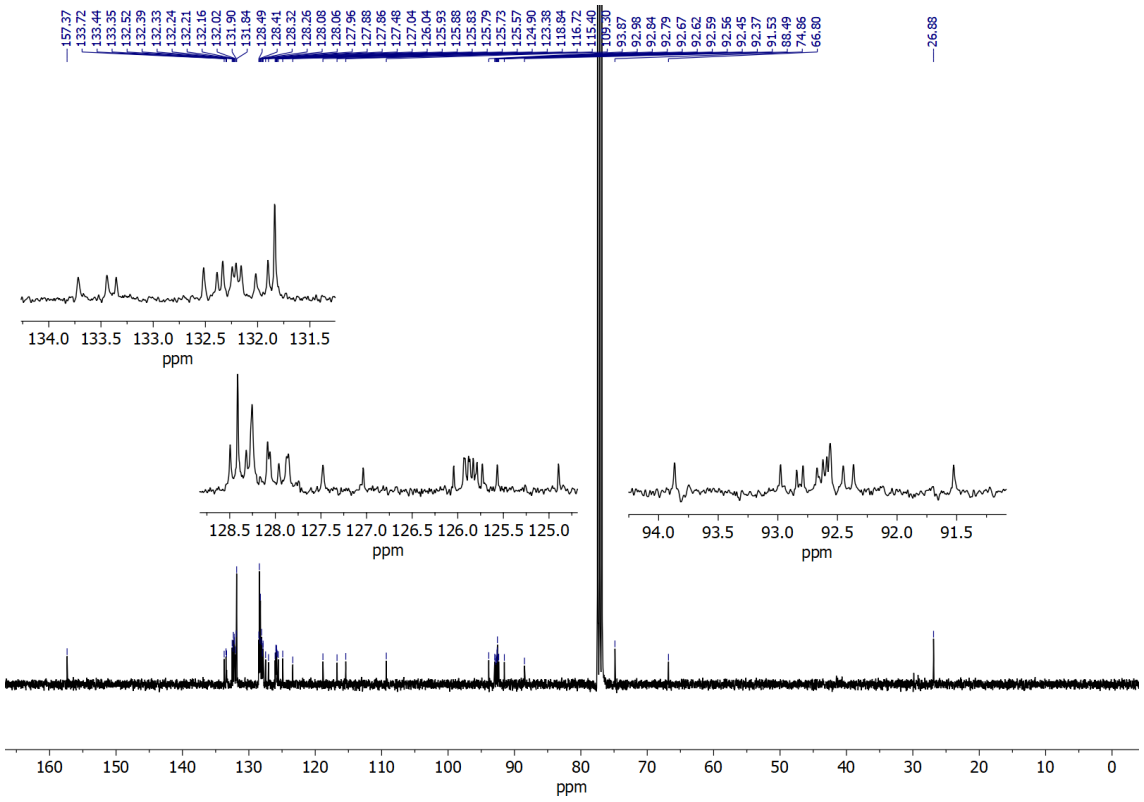


Figure S18. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound (*S*,*S*,*P*)-**6.**

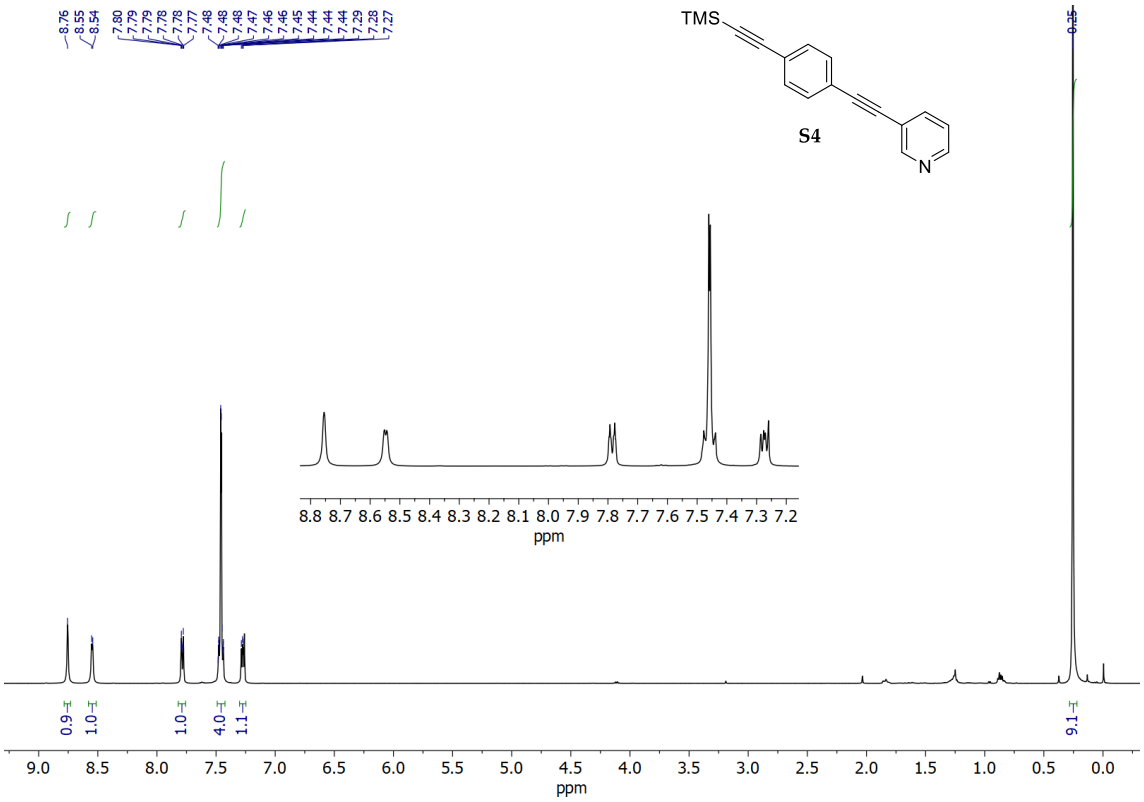


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **S4**.

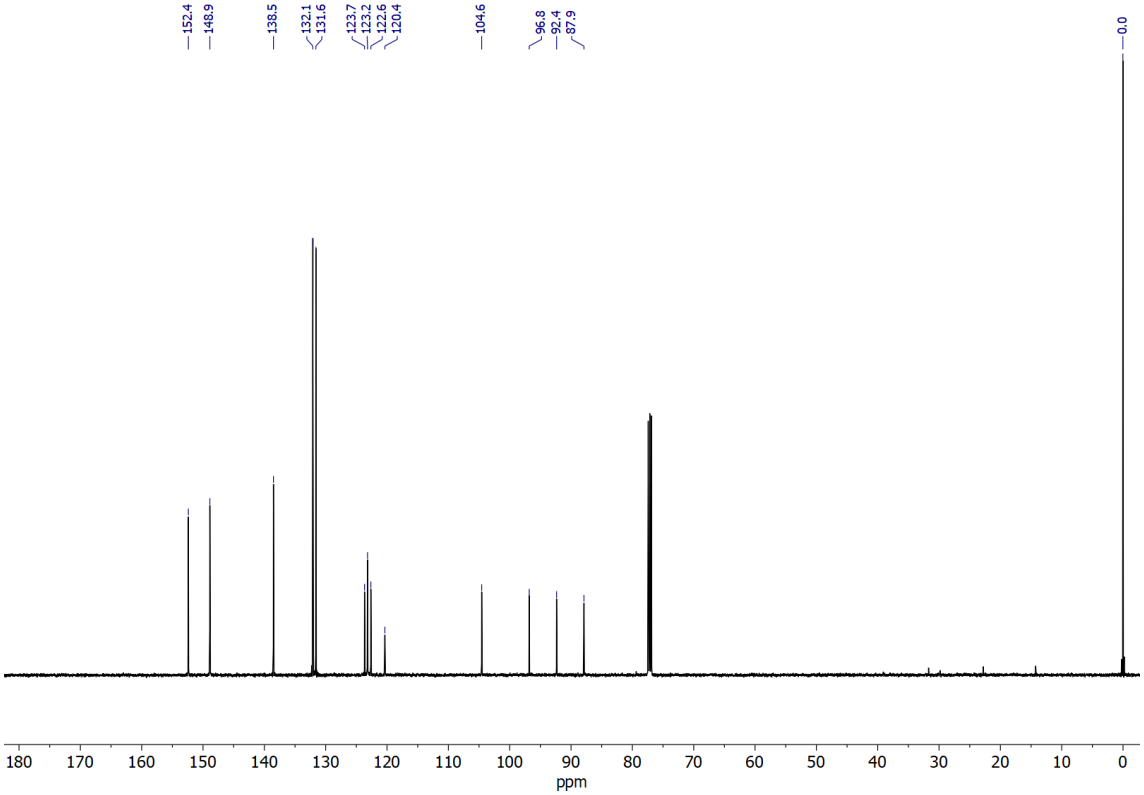


Figure S20. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **S4**.

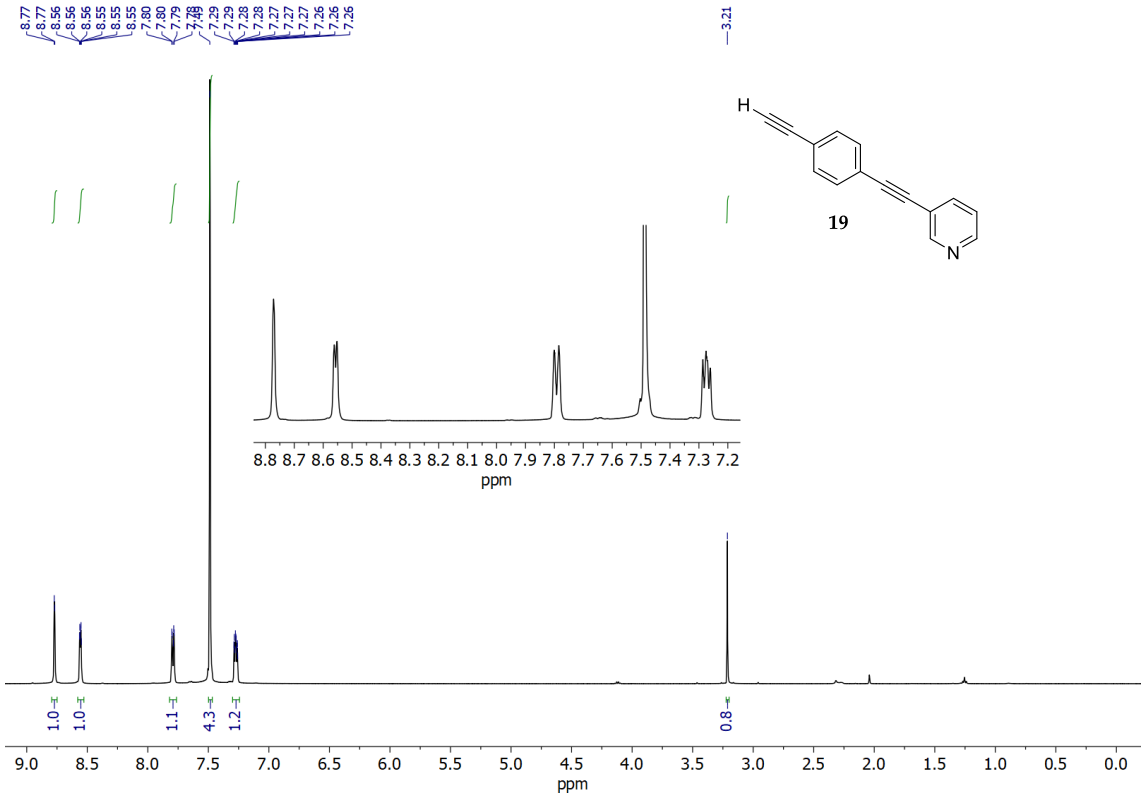


Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **19**.

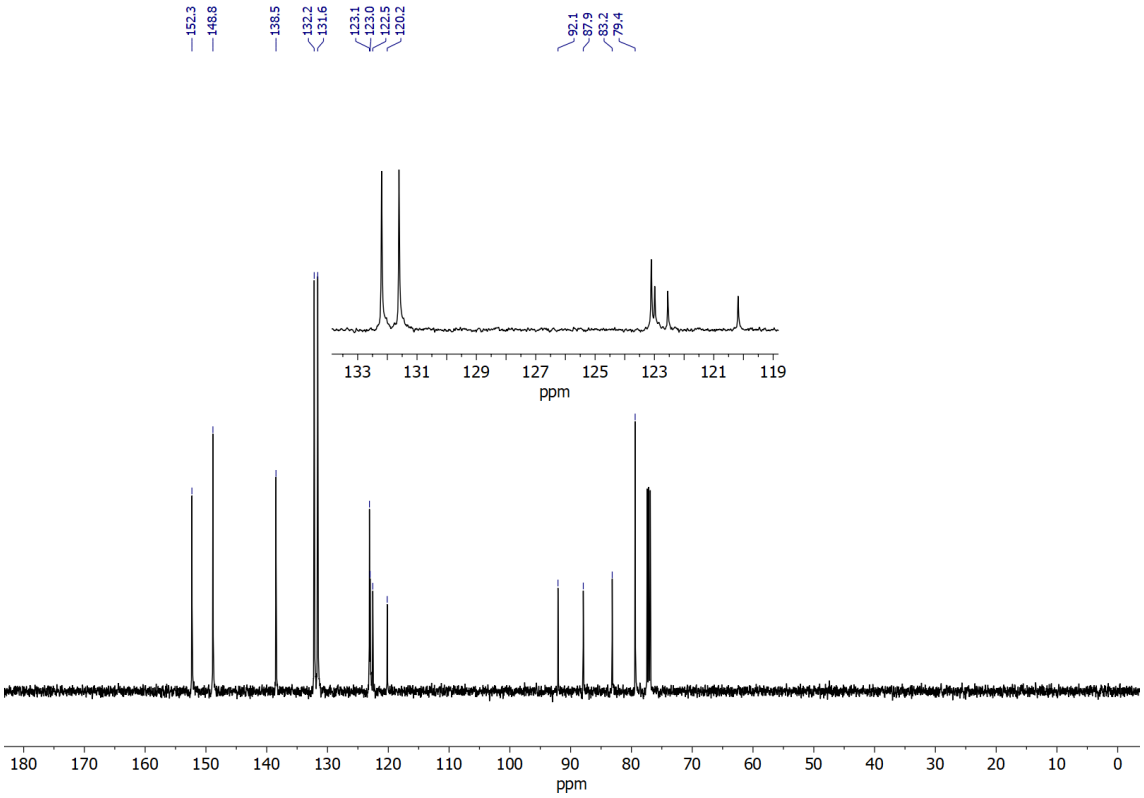


Figure S22. ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound **19**.

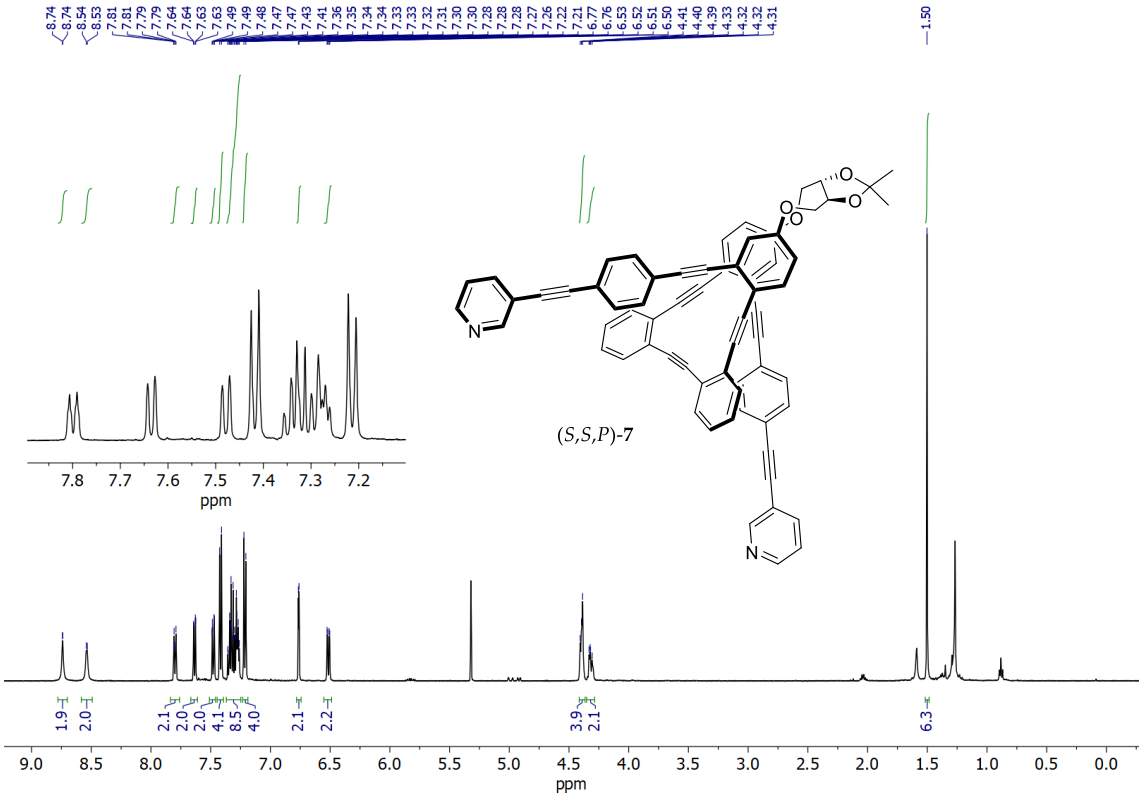


Figure S23. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of compound (*S*,*S*,*P*)-**7**.

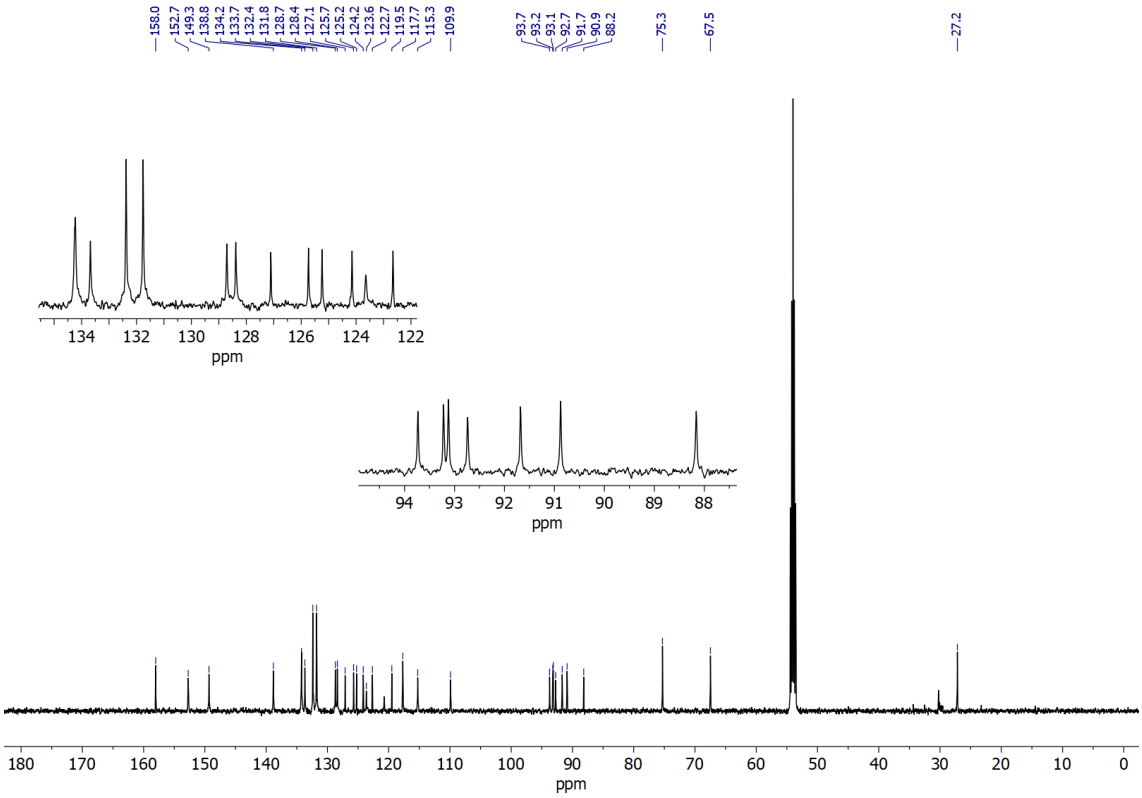


Figure S24. ^{13}C NMR (126 MHz, CD_2Cl_2) spectrum of compound (*S*,*S*,*P*)-**7**.

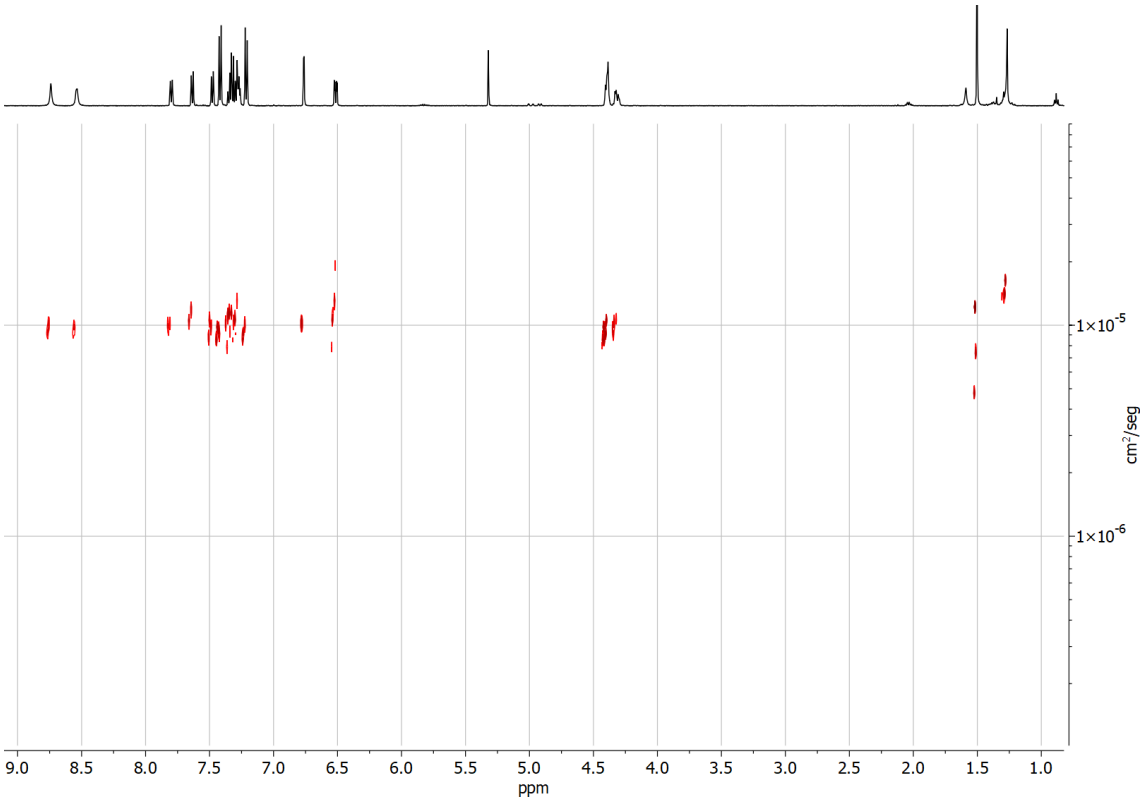


Figure S25. DOSY NMR (500 MHz, CD_2Cl_2) spectrum of (*S*,*S*,*P*)-**7**.

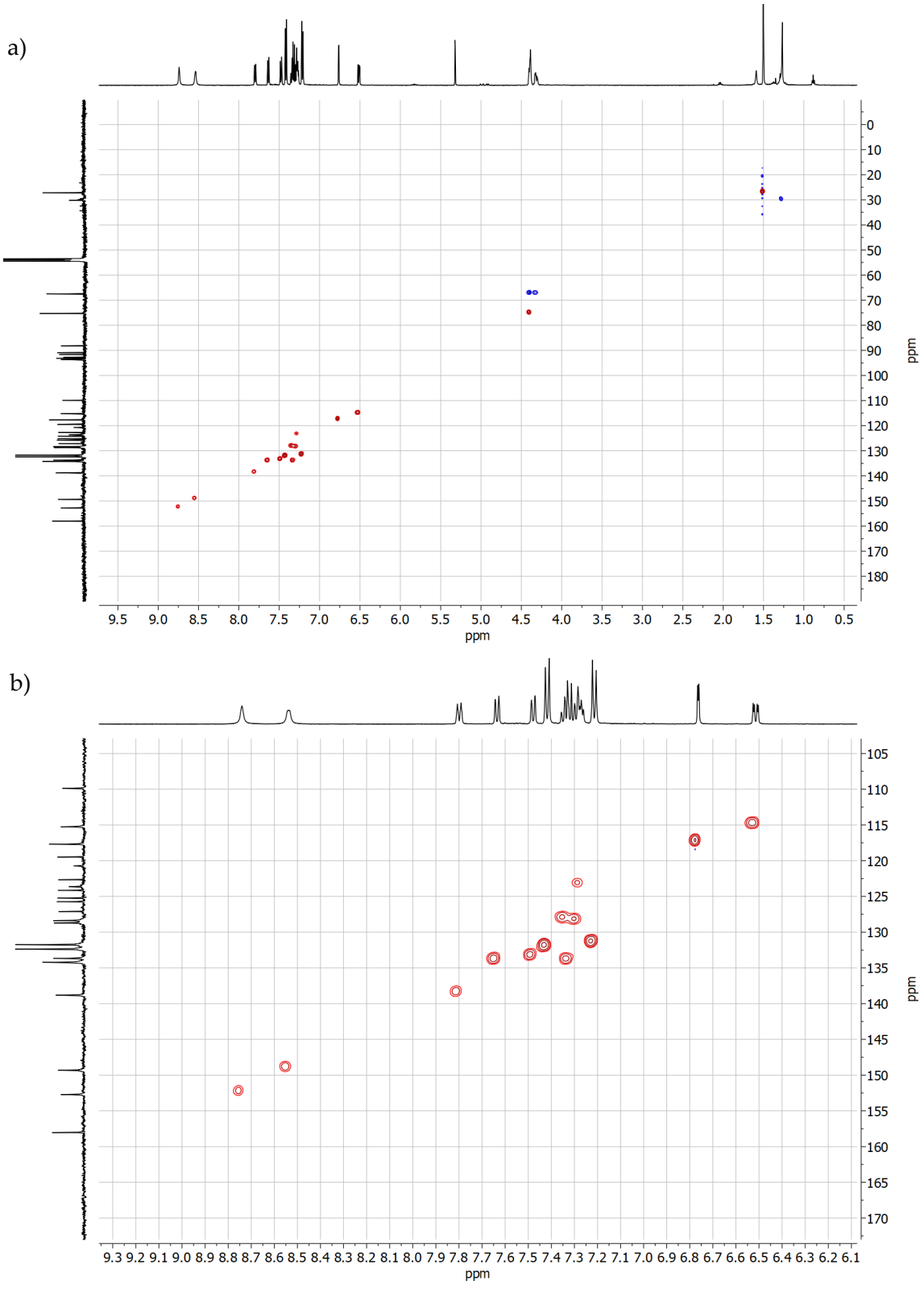


Figure S26. a) Complete and **b)** partial HSQC NMR (500 MHz and 126 MHz, CD_2Cl_2) spectrum of (*S*,*S*,*P*)-**7**.

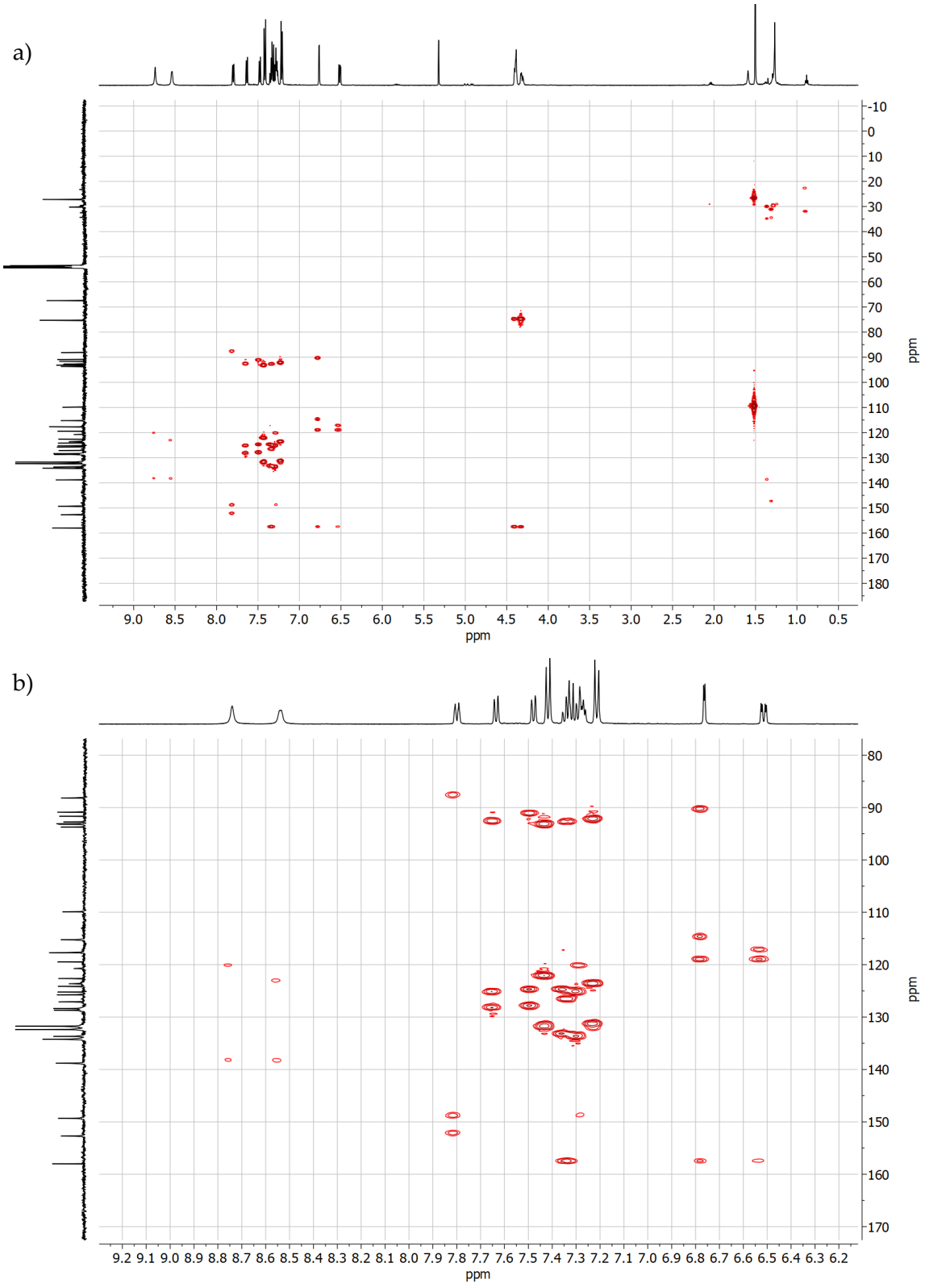


Figure S27. a) Complete and **b)** partial HMBC NMR (500 MHz and 126 MHz, CD_2Cl_2) spectrum of (*S*,*S*,*P*)-**7**.

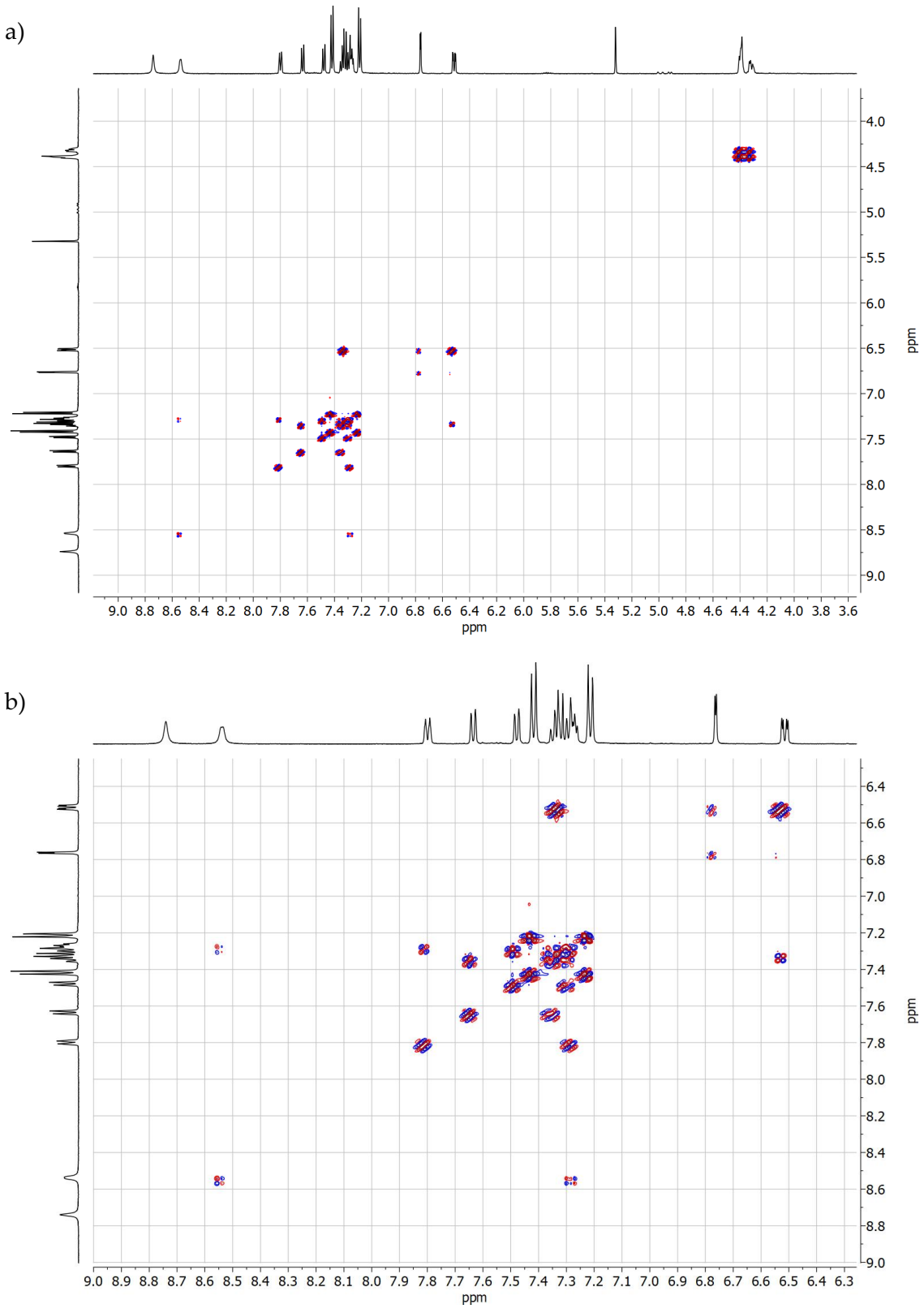


Figure S28. a) Complete and **b)** partial COSY NMR (500 MHz, CD_2Cl_2) spectrum of (*S*,*S*,*P*)-**7**.

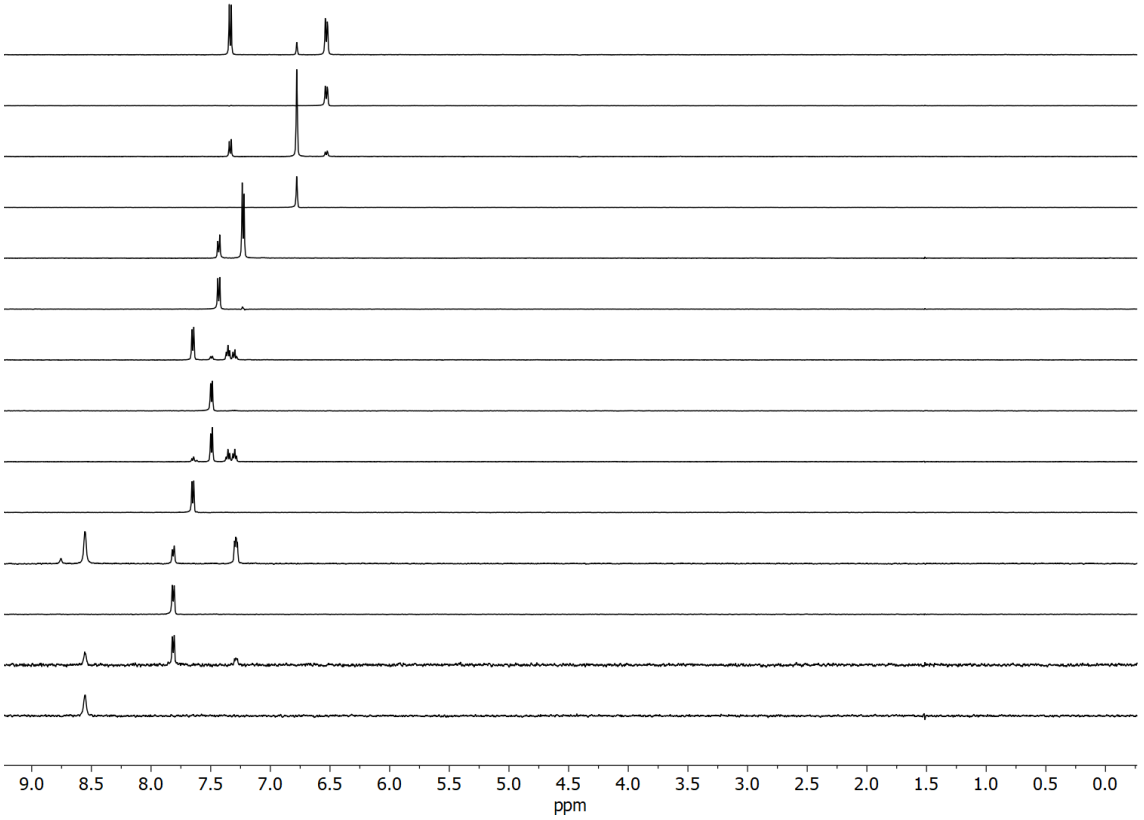


Figure S29. TOCSY NMR (500 MHz, CD_2Cl_2) spectrum of compound (*S*,*S*,*P*)-**7**.

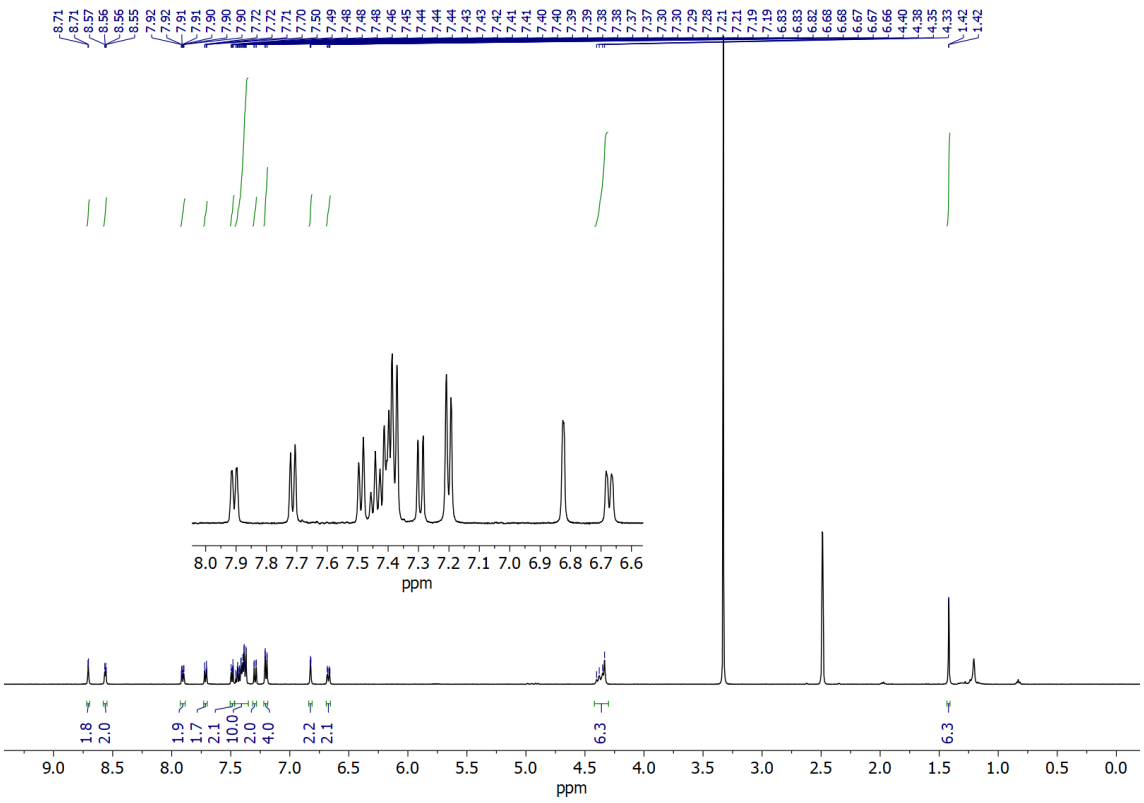


Figure S30. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound (*S*,*S*,*P*)-**7**.

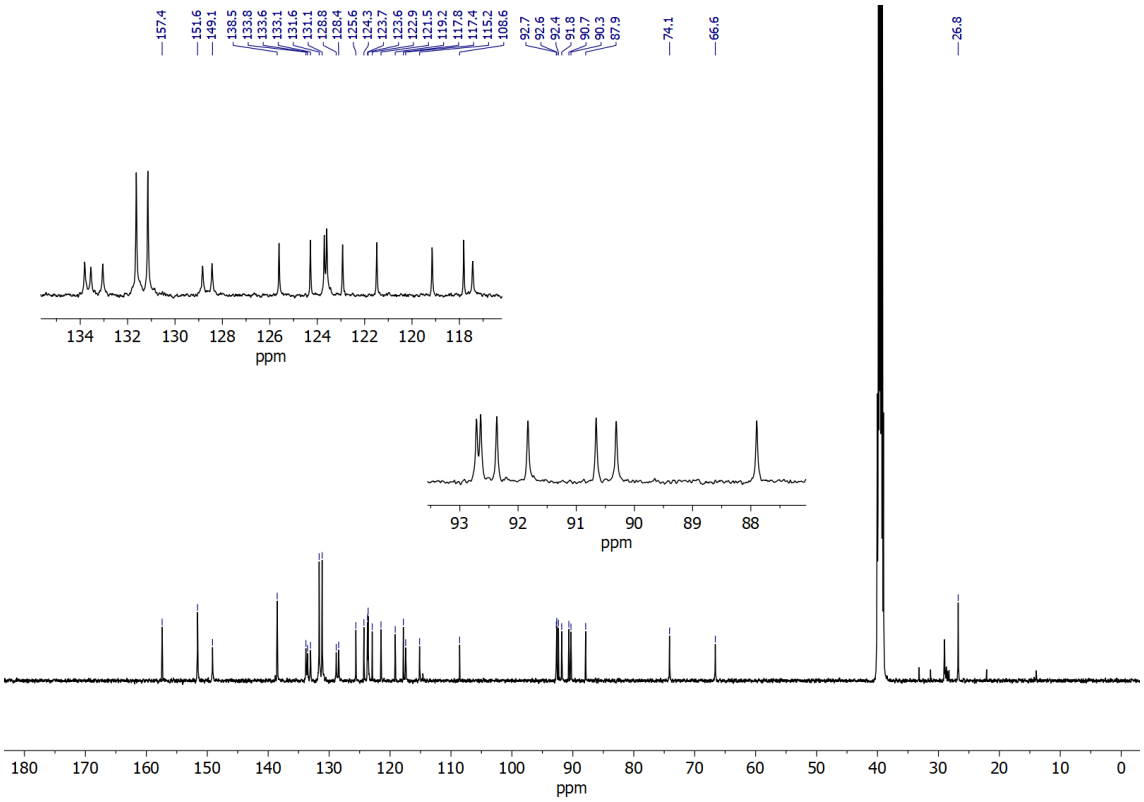


Figure S31. ^{13}C NMR (126 MHz, DMSO-d_6) spectrum of compound (*S*,*S*,*P*)-**7**.

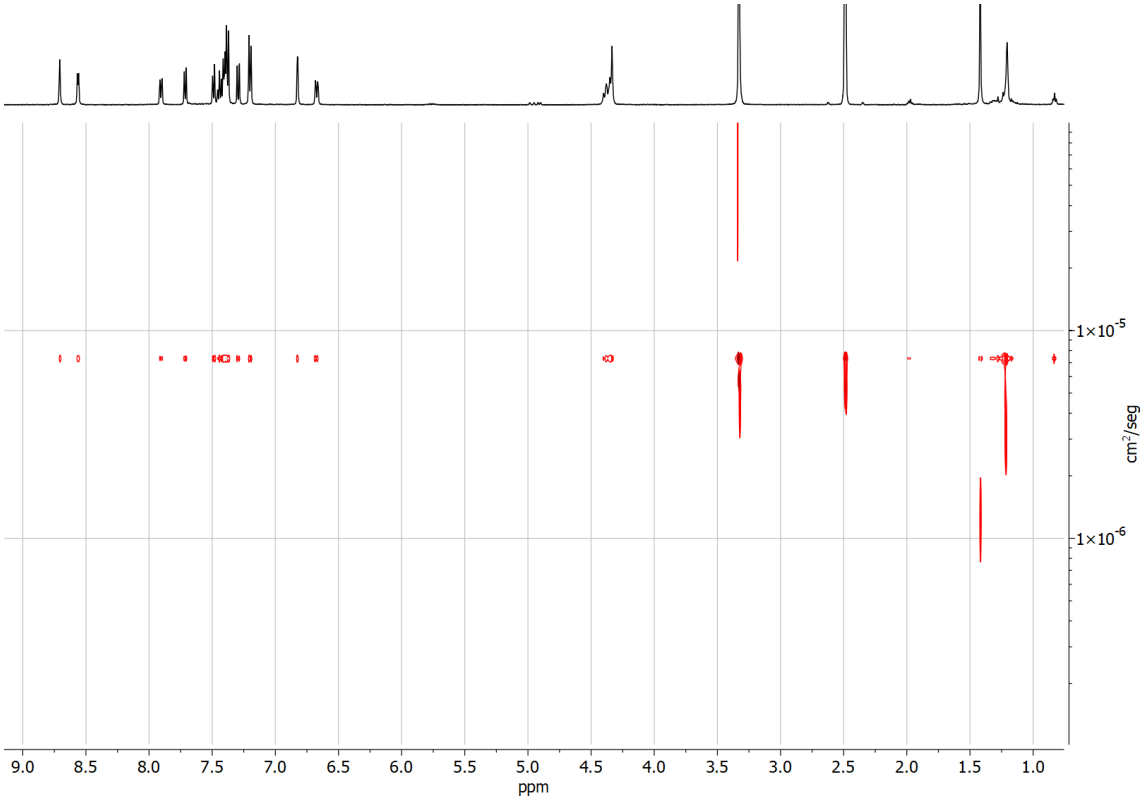


Figure S32. DOSY NMR (500 MHz, DMSO-d_6) spectrum of (*S*,*S*,*P*)-**7**.

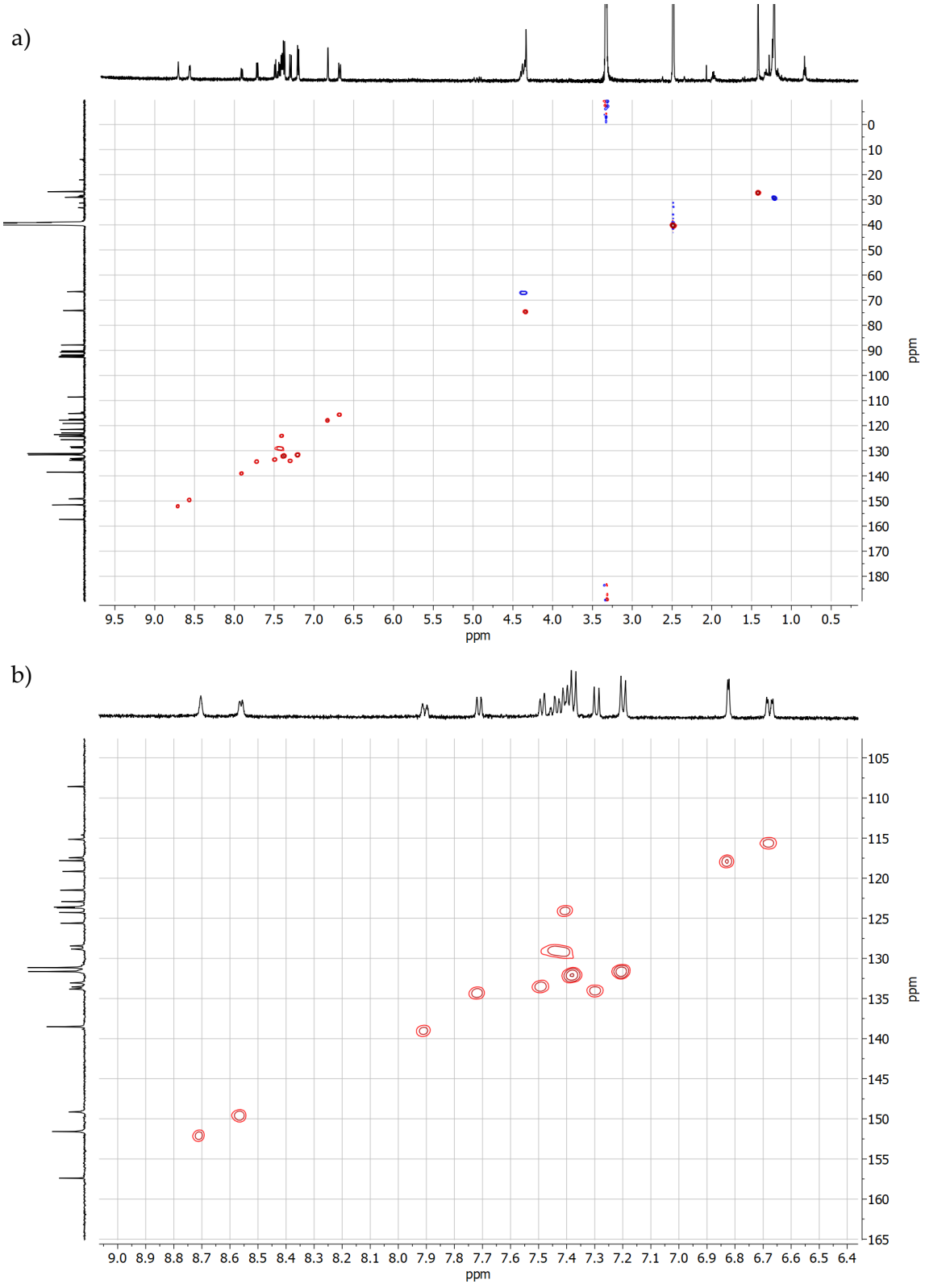


Figure S33. a) Complete and **b)** partial HSQC NMR (500 MHz and 126 MHz, DMSO-d_6) spectrum of (*S*,*S*,*P*)-**7**.

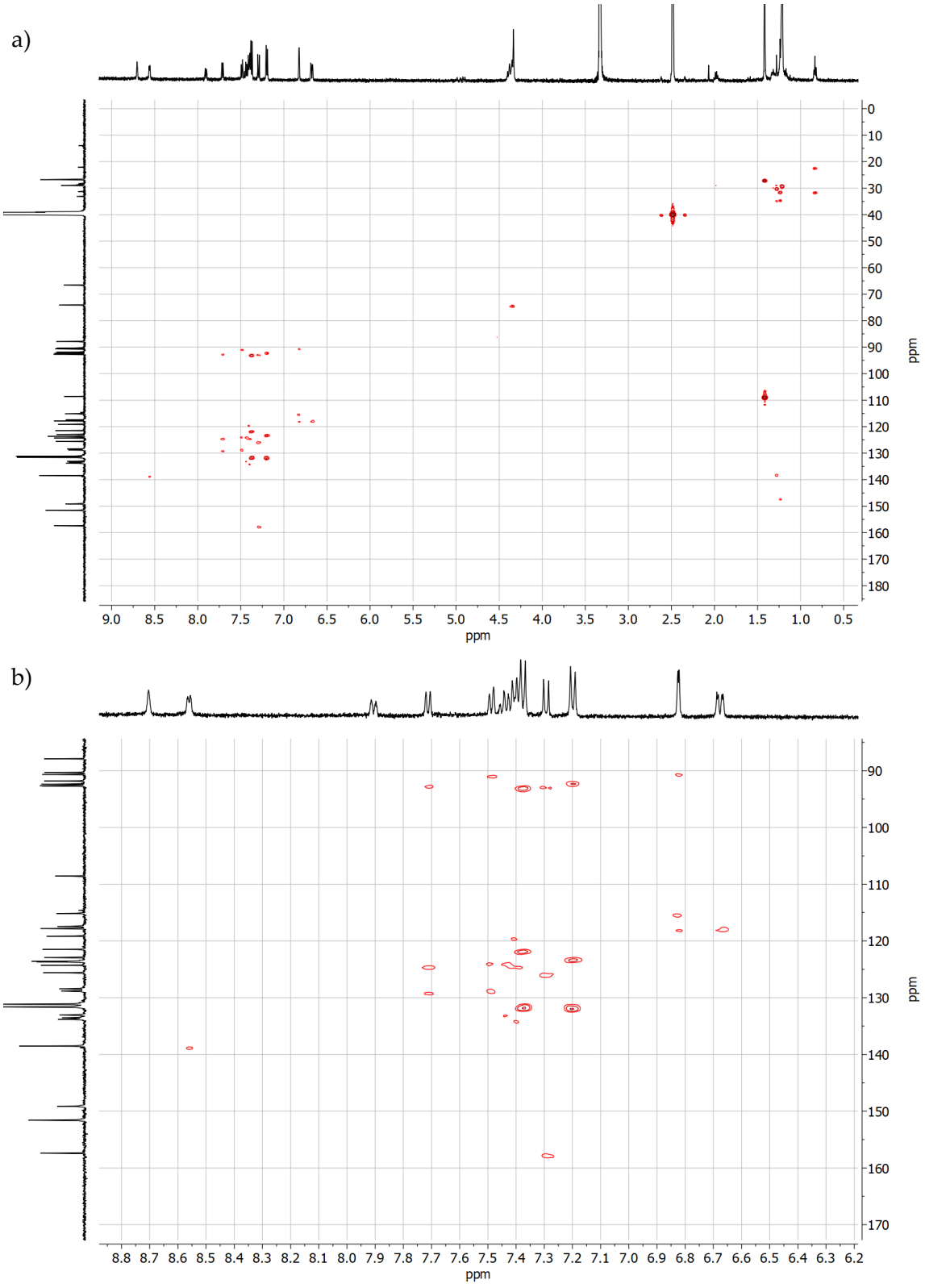


Figure S34. a) Complete and **b)** partial HMBC NMR (500 MHz and 126 MHz, DMSO-d_6) spectrum of (*S*,*S*,*P*)-**7**.

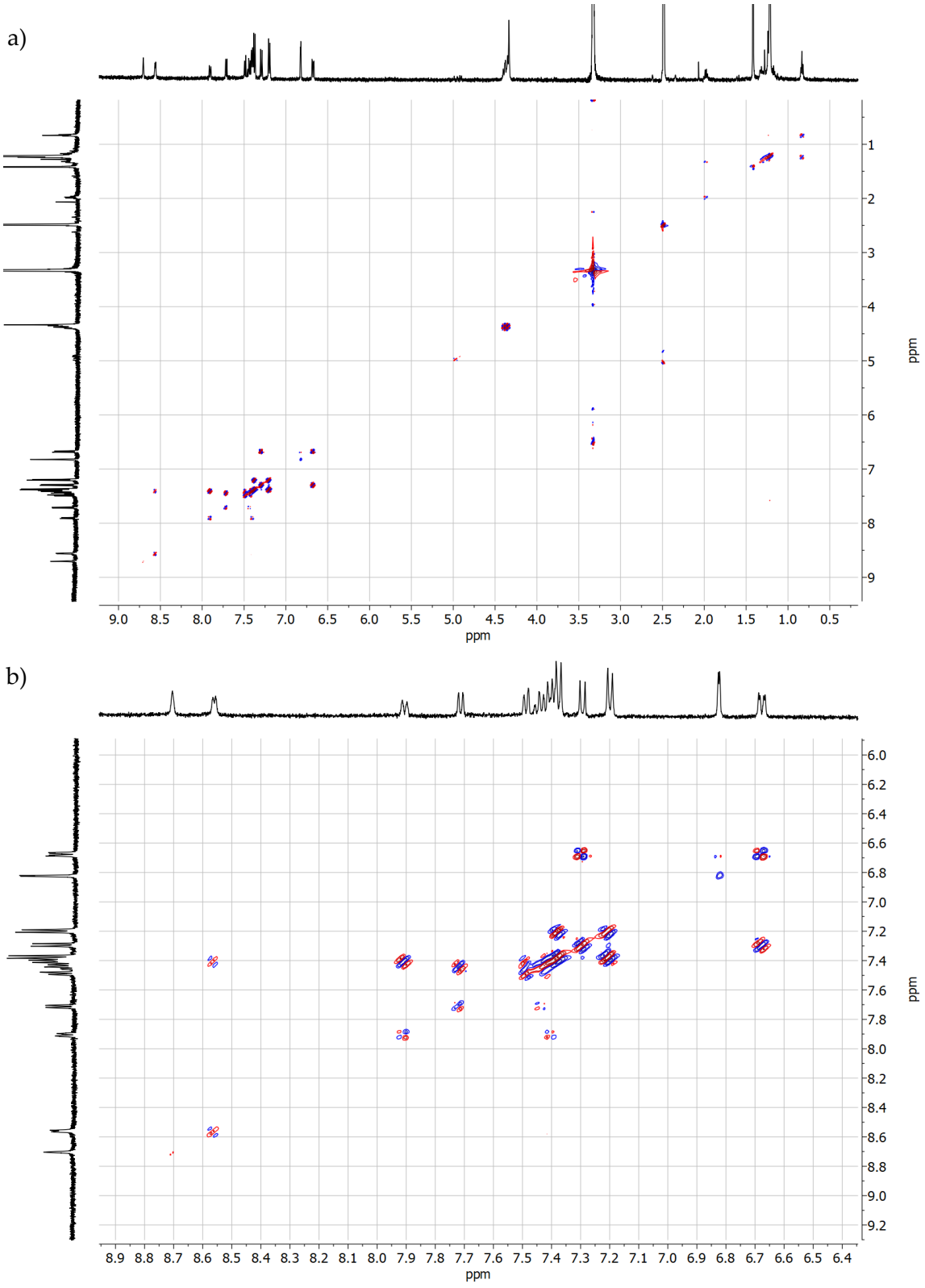


Figure S35. a) Complete and **b)** partial COSY NMR (500 MHz, DMSO-d_6) spectrum of (*S*,*S*,*P*)-**7**.

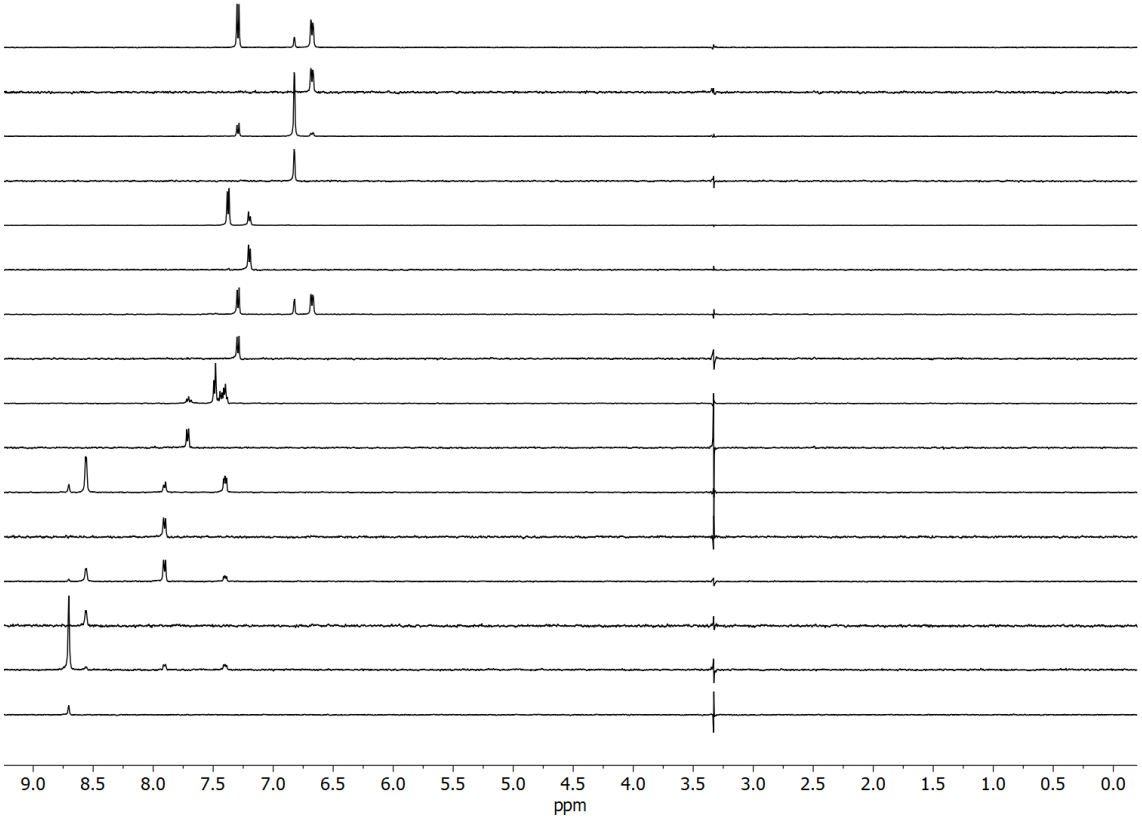


Figure S36. TOCSY NMR (500 MHz, DMSO-d_6) spectrum of compound (*S*,*S*,*P*)-**7**.

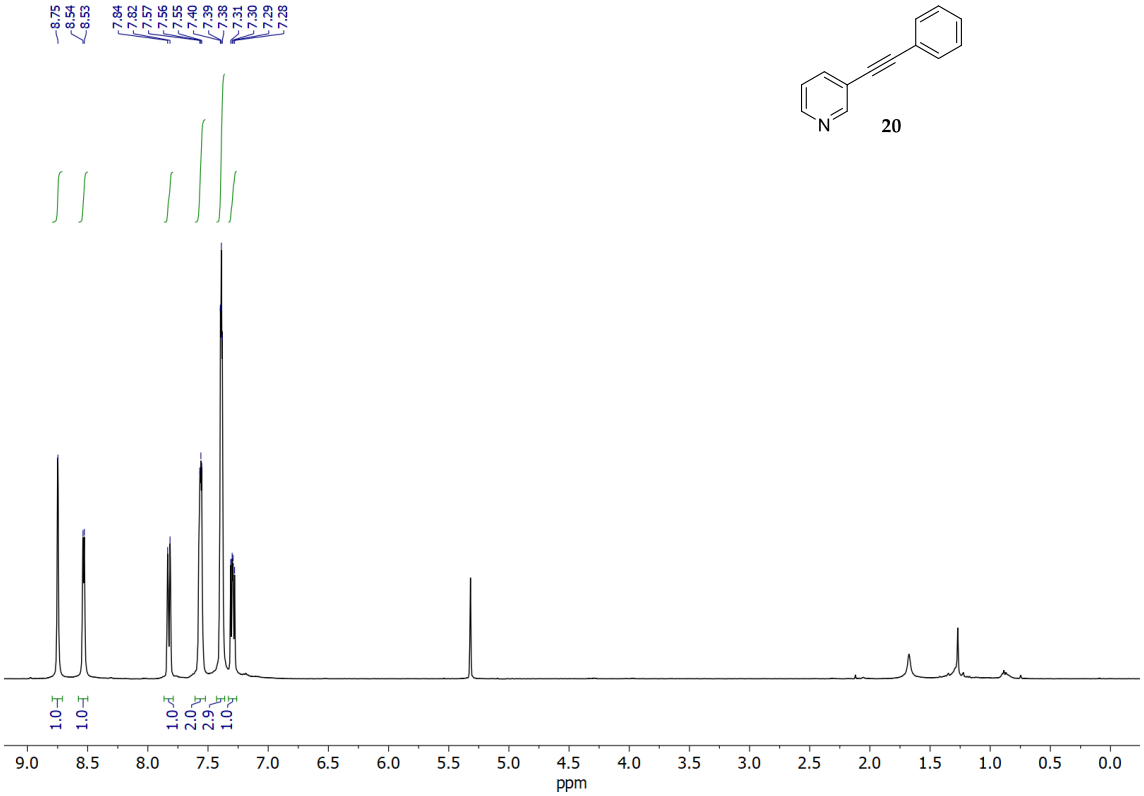


Figure S37. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of compound **20**.

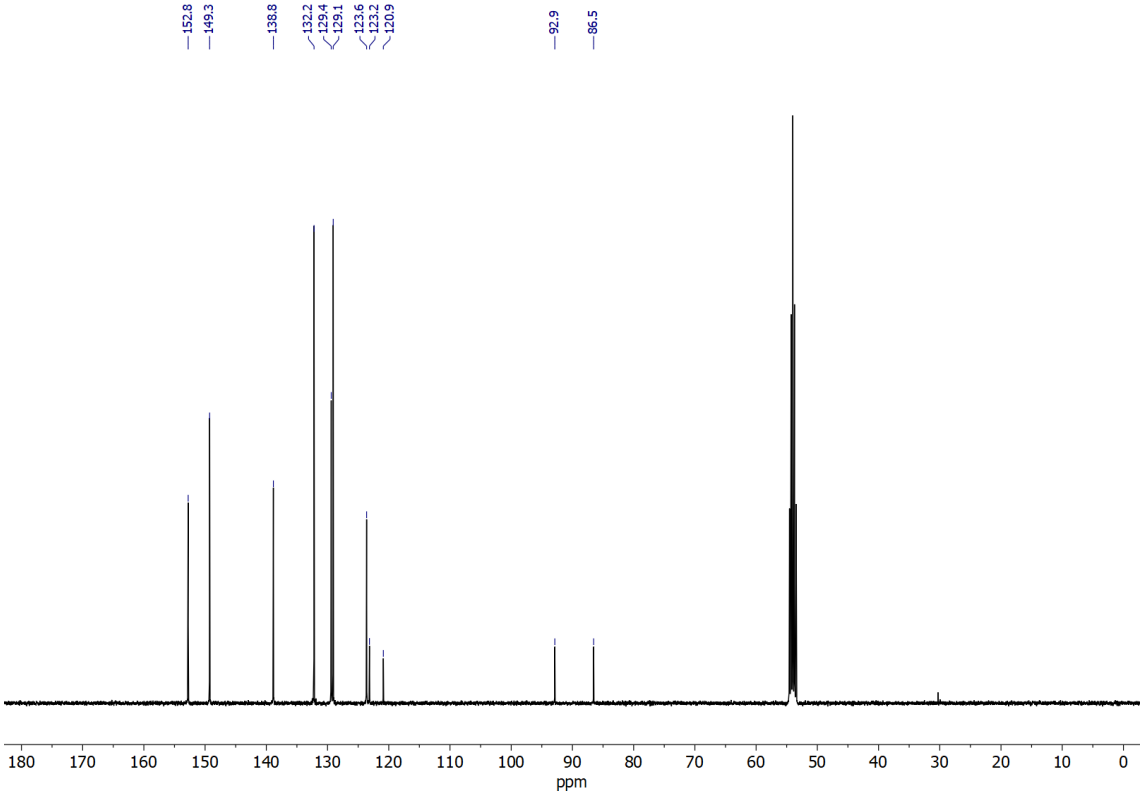


Figure S38. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of compound **20**.

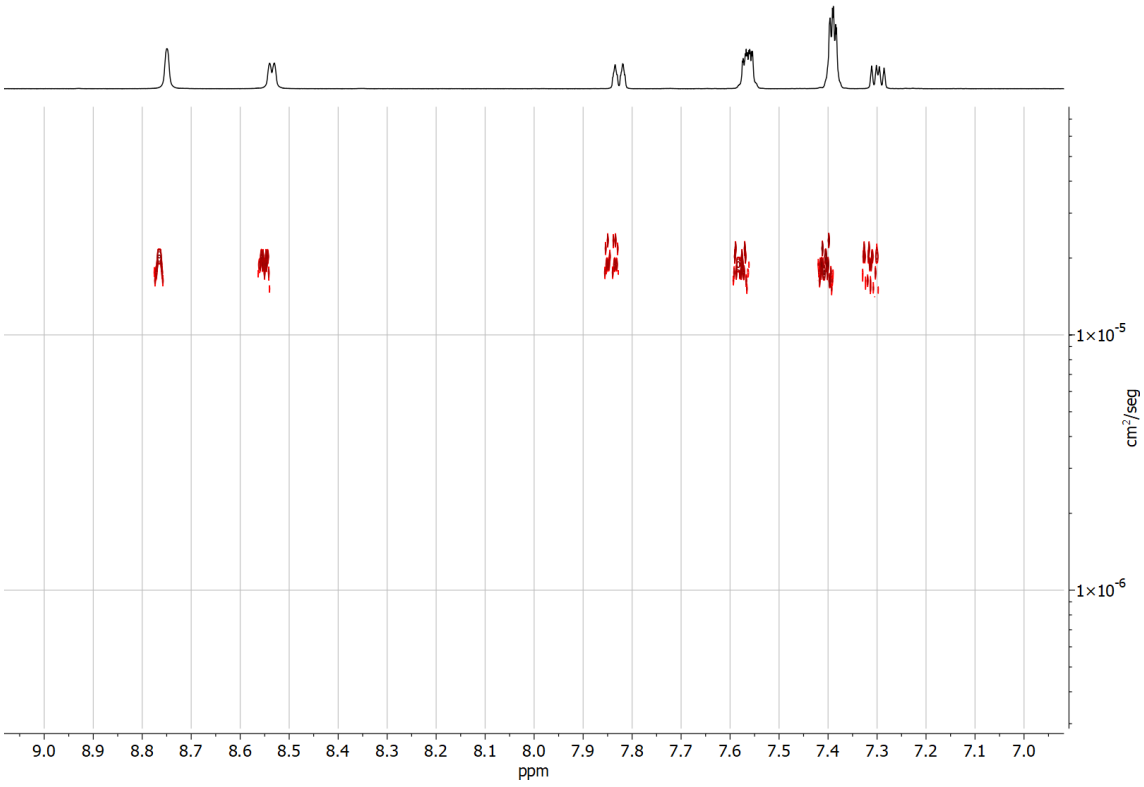


Figure S39. DOSY NMR (500 MHz, CD_2Cl_2) spectrum of **20**.

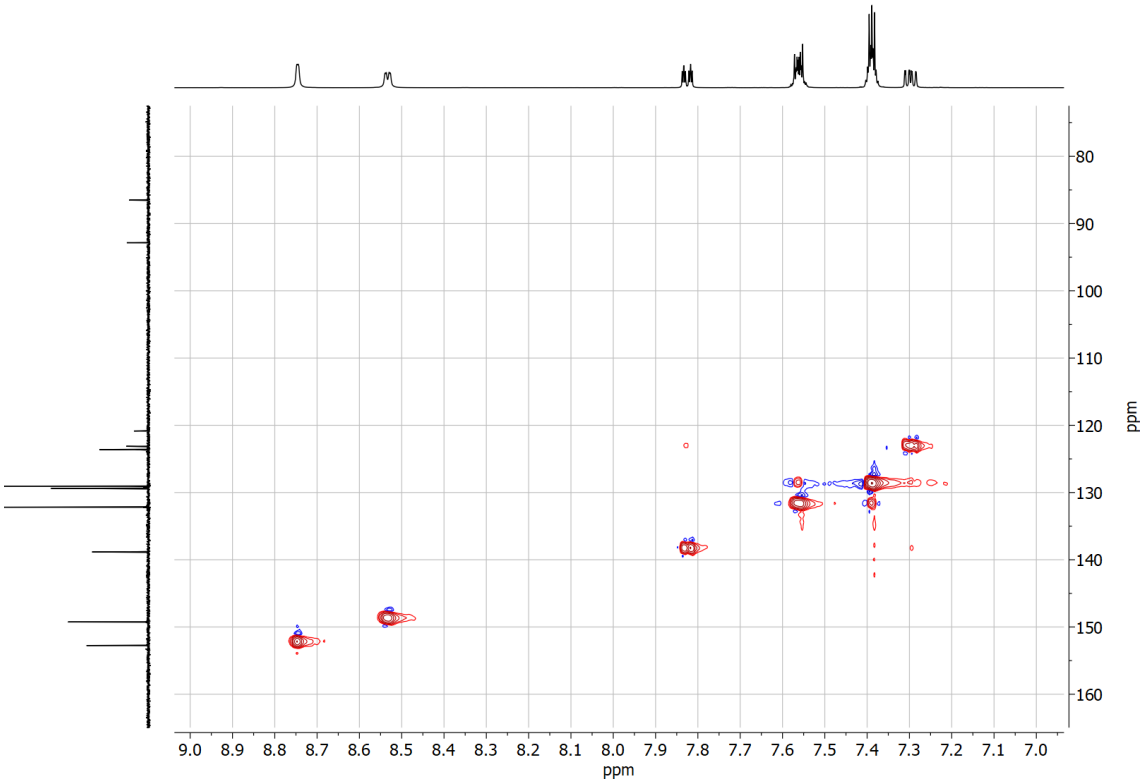


Figure S40. HSQC NMR (500 MHz and 126 MHz, CD_2Cl_2) spectrum of **20**.

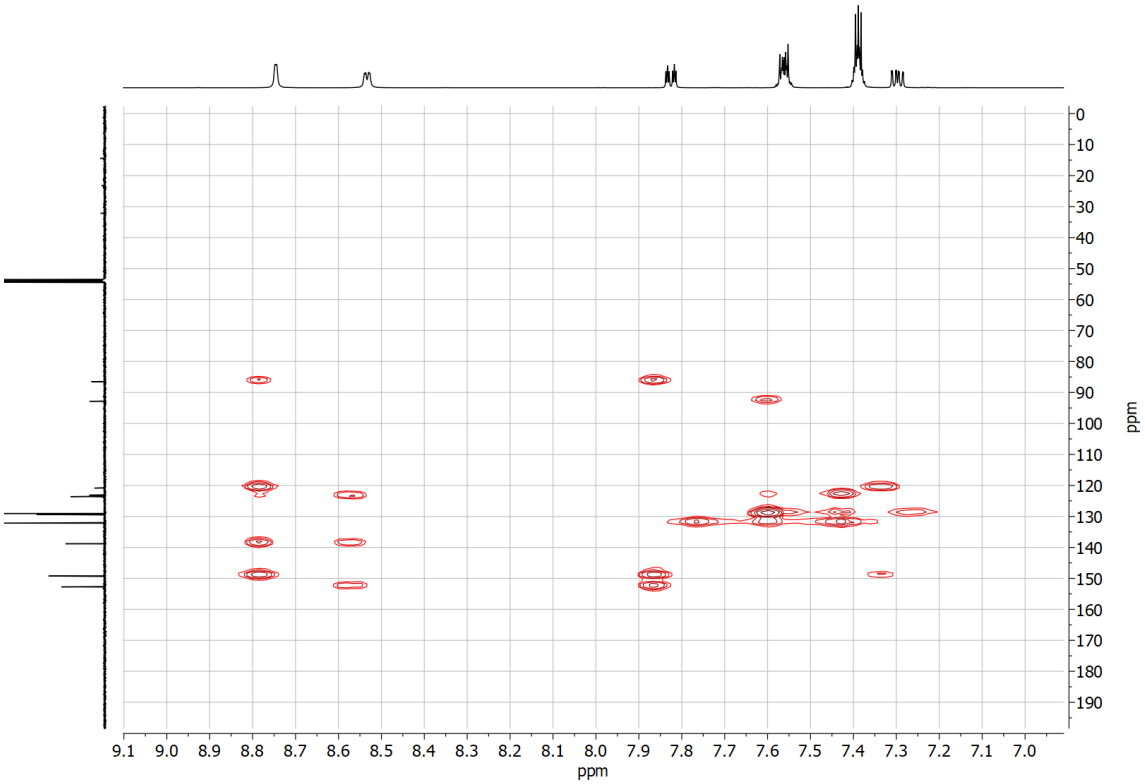


Figure S41. HMBC NMR (500 MHz and 126 MHz, CD_2Cl_2) spectrum of **20**.

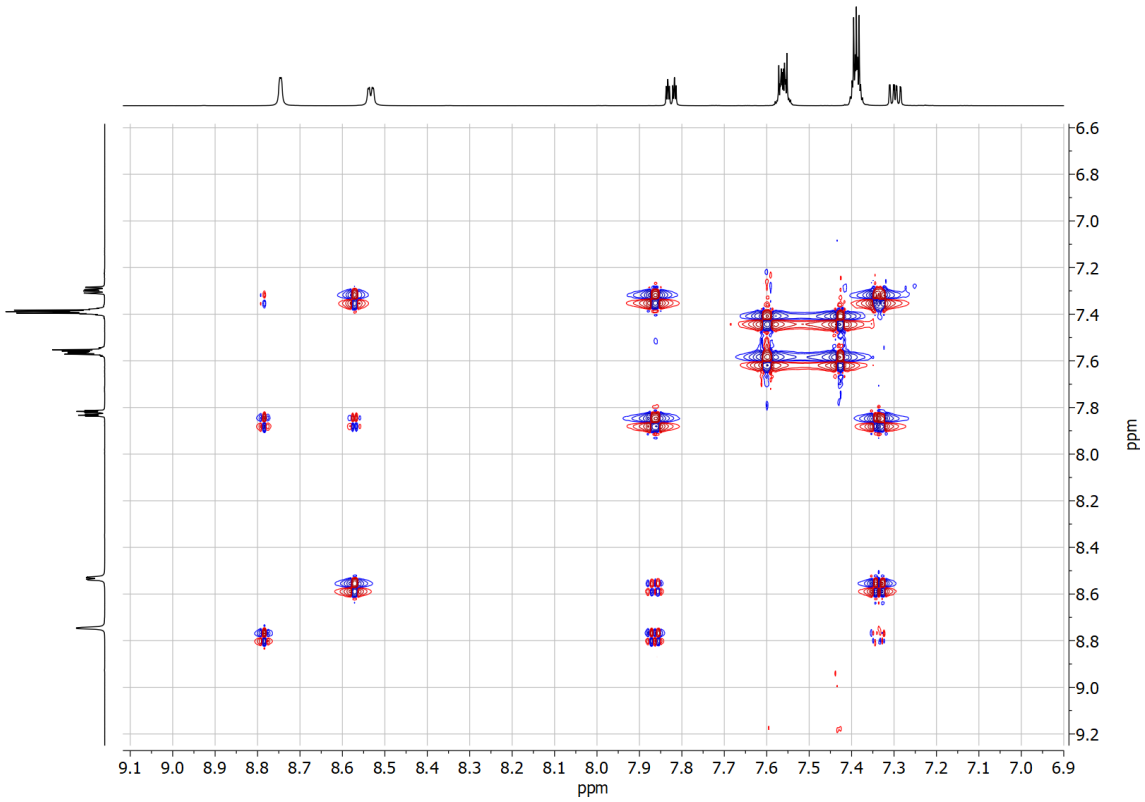


Figure S42. COSY NMR (500 MHz, CD_2Cl_2) spectrum of **20**.

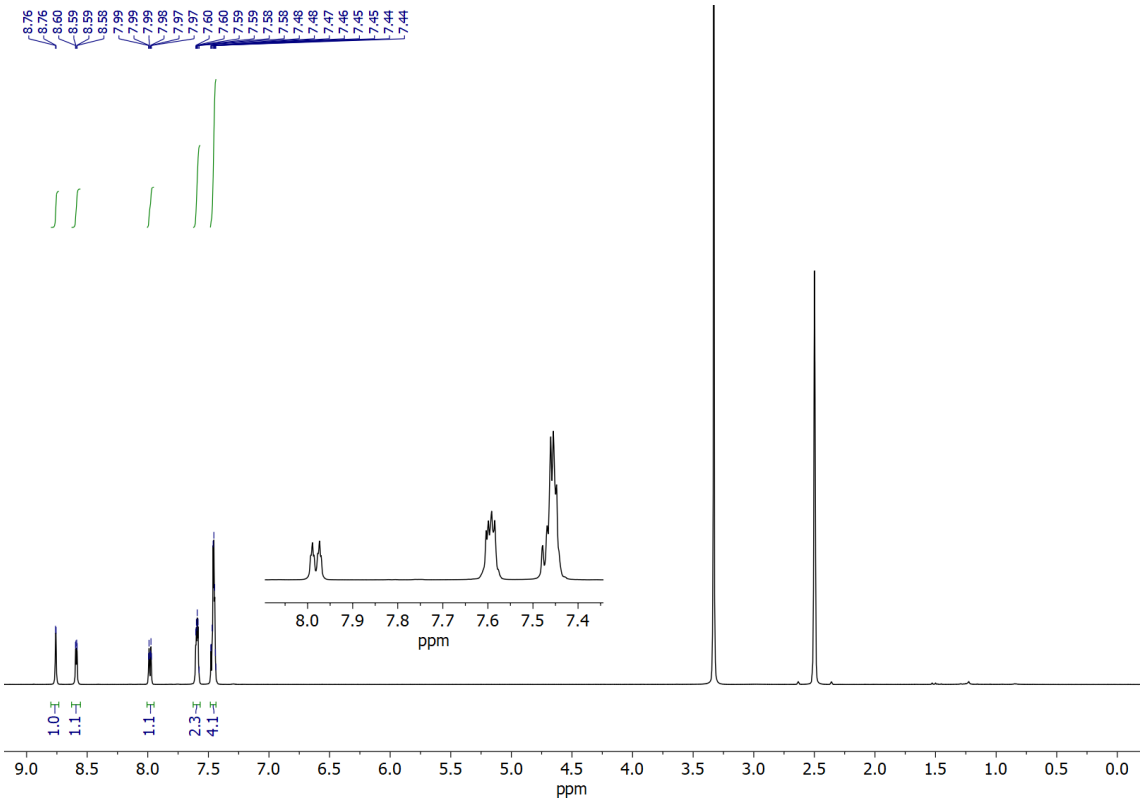


Figure S43. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of compound **20**.

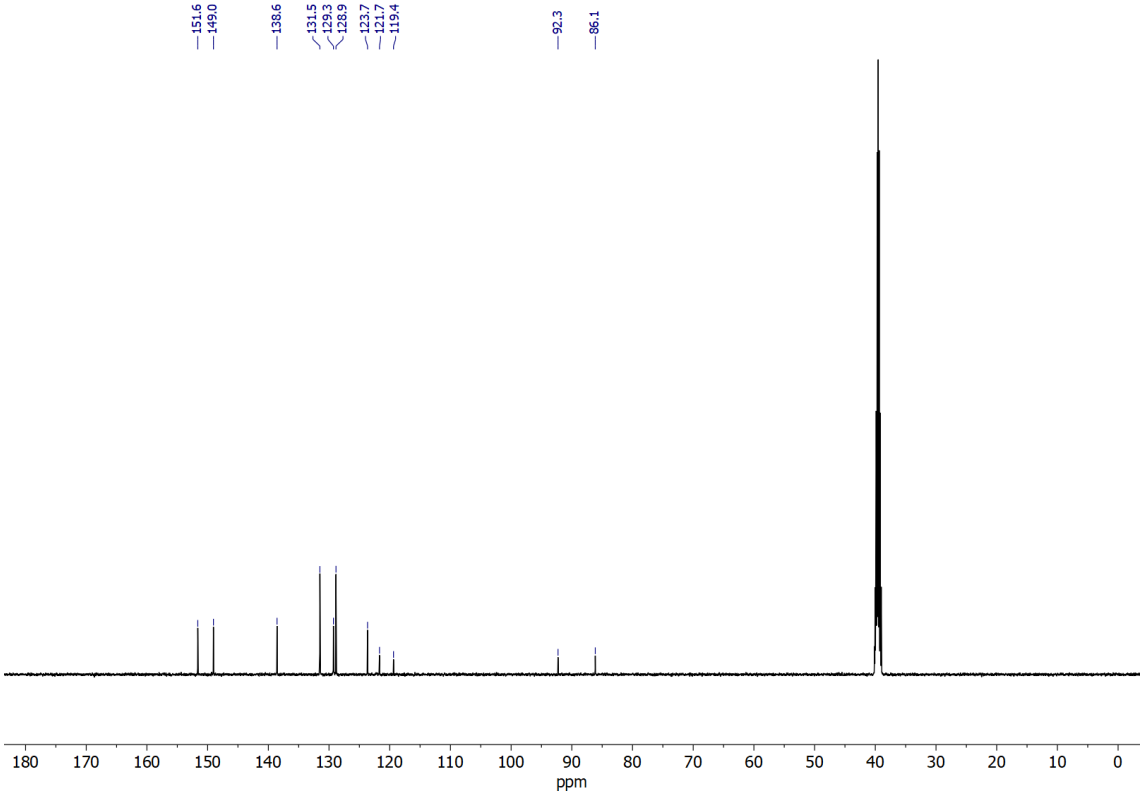


Figure S44. ^{13}C NMR (126 MHz, DMSO-d_6) spectrum of compound **20**.

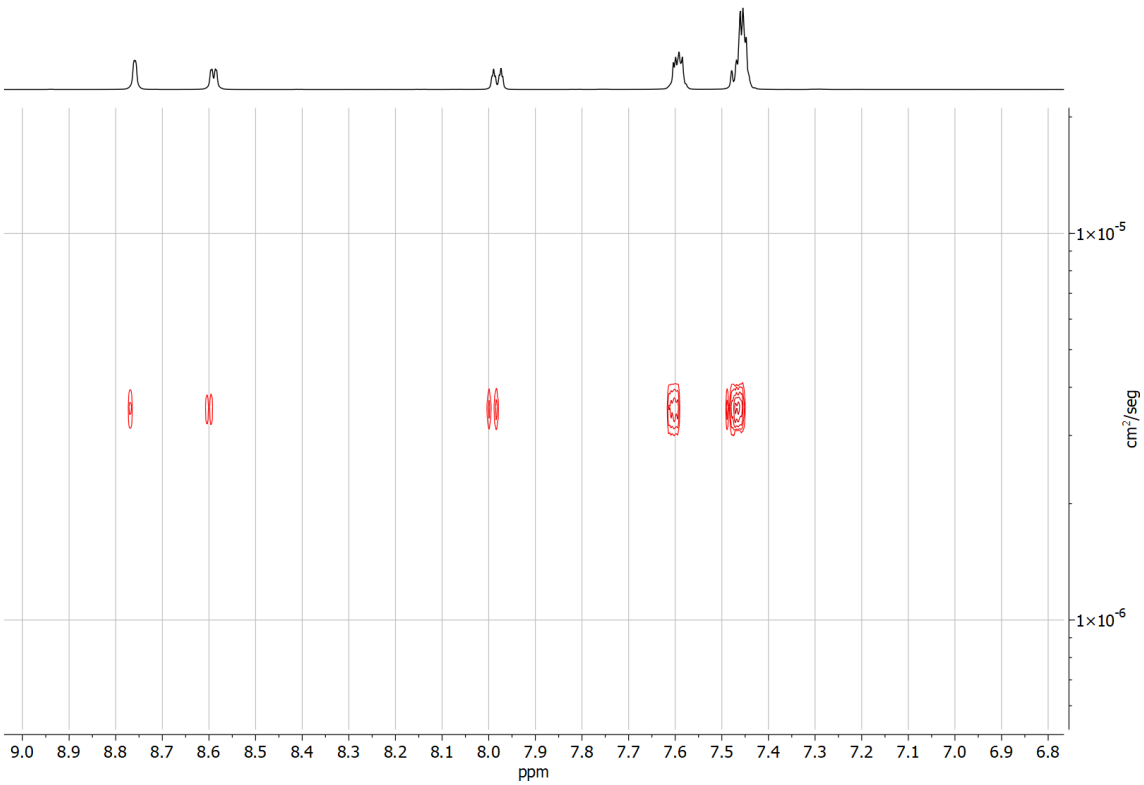


Figure S45. DOSY NMR (500 MHz, DMSO-d_6) spectrum of **20**.

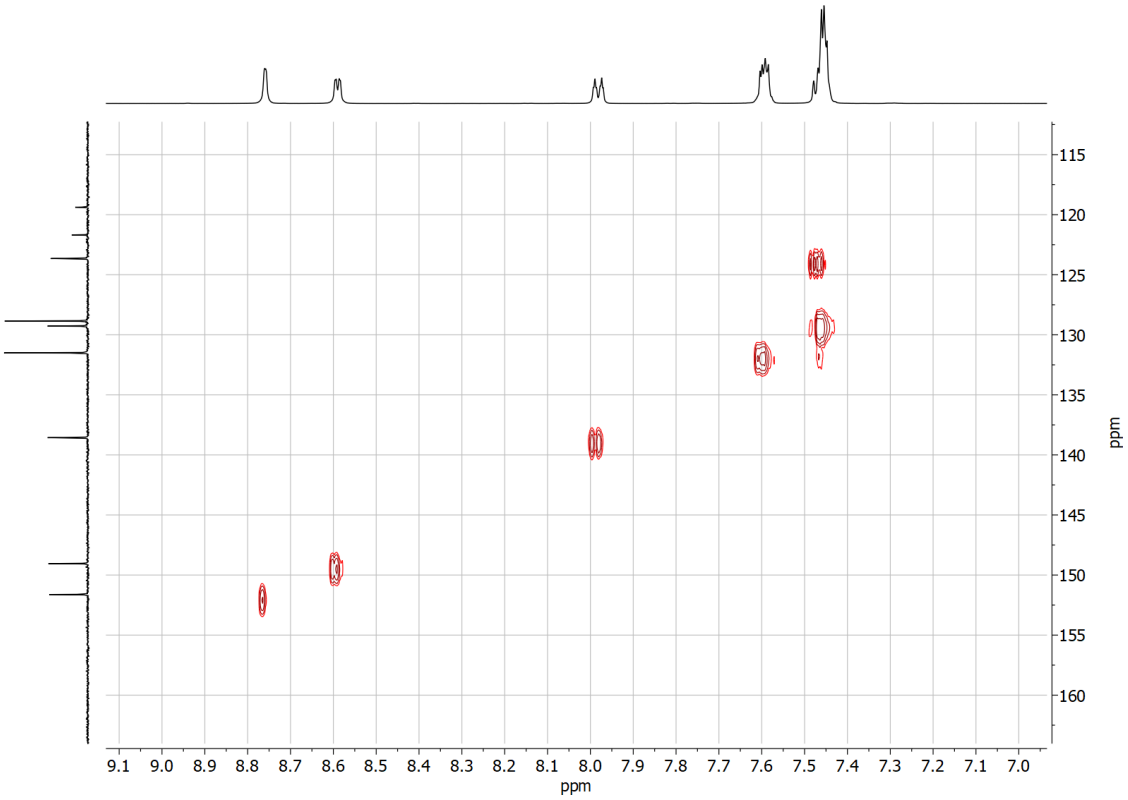


Figure S46. HSQC NMR (500 MHz and 126 MHz, DMSO-d_6) spectrum of **20**.

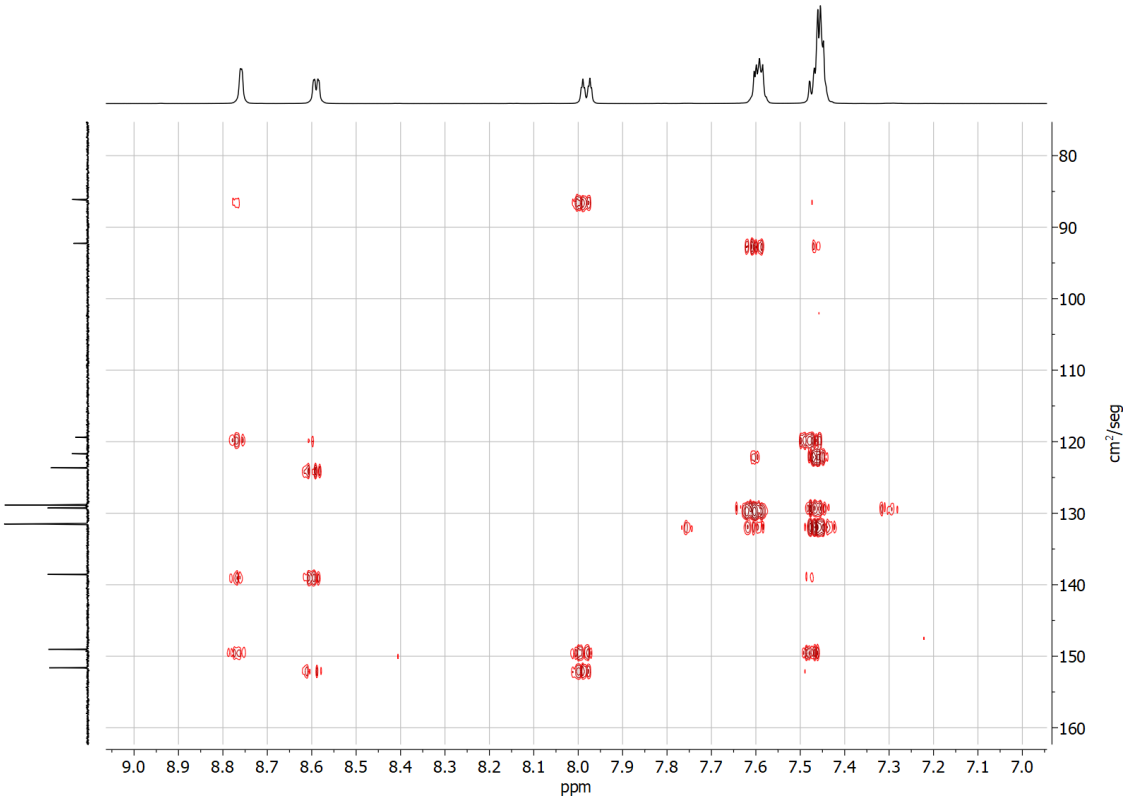


Figure S47. HMBC NMR (500 MHz and 126 MHz, DMSO-d_6) spectrum of **20**.

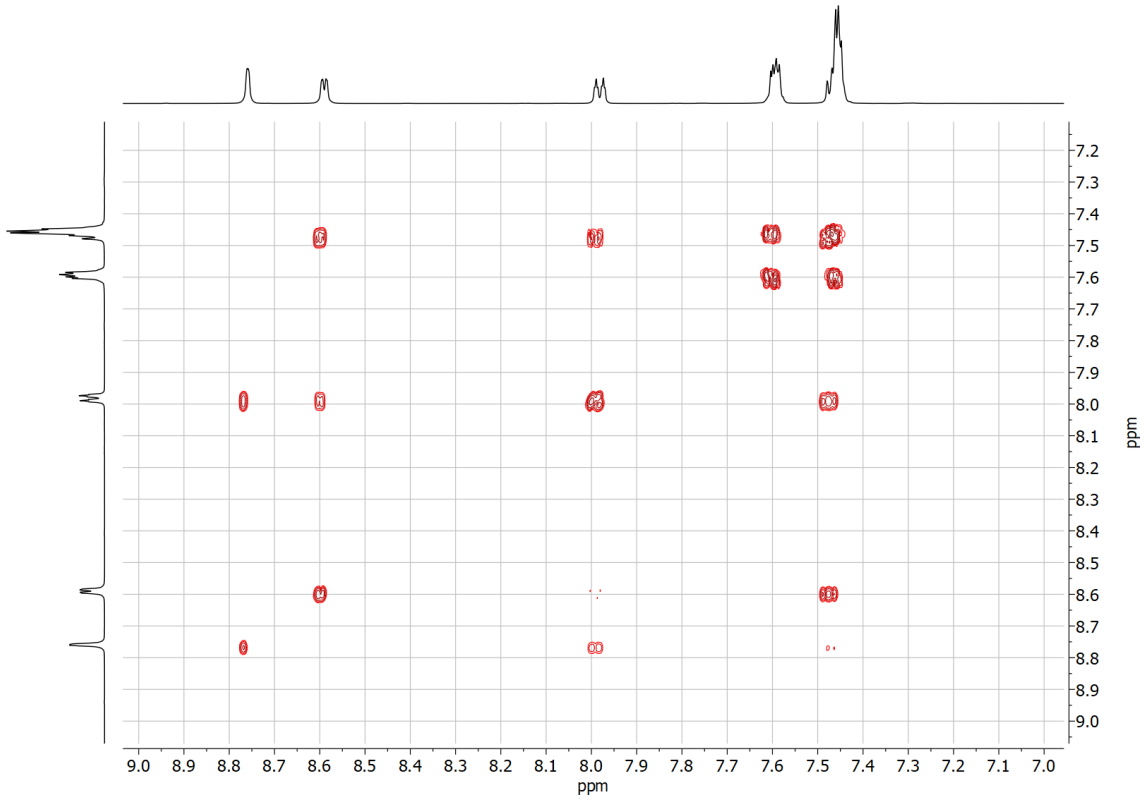


Figure S48. COSY NMR (500 MHz, DMSO-d_6) spectrum of **20**.

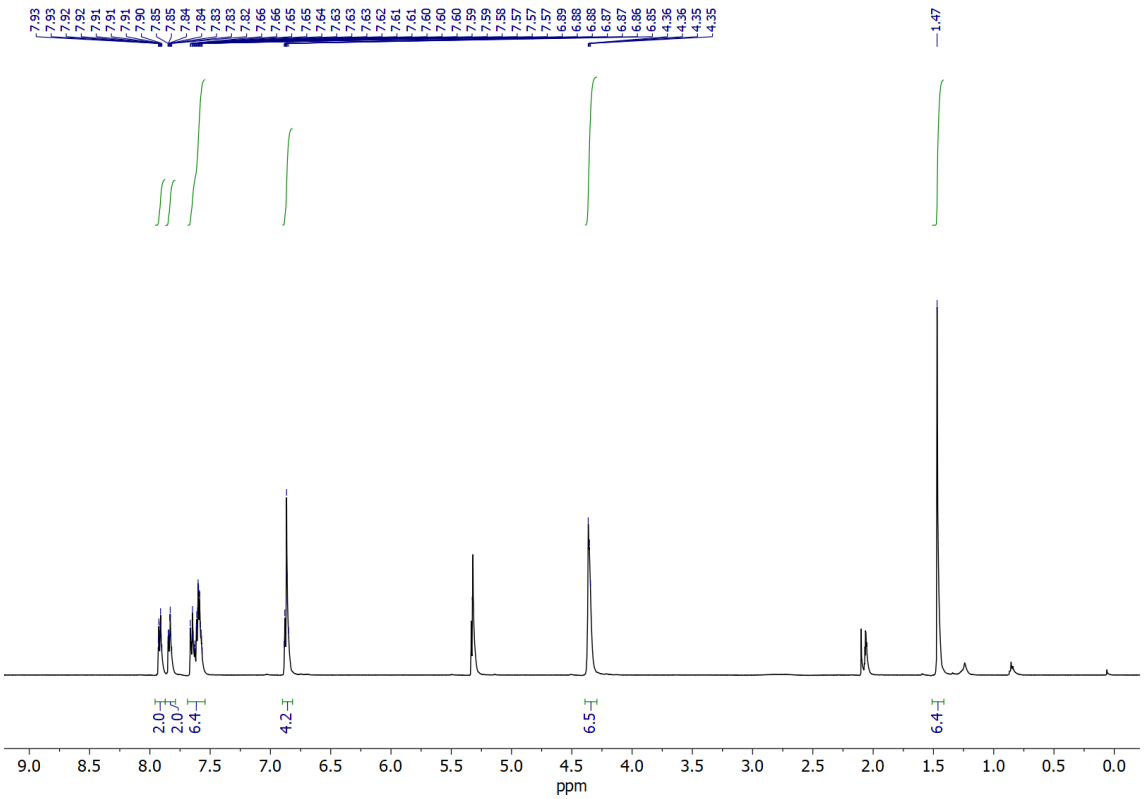


Figure S49. ^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-1:Ag(I)**.

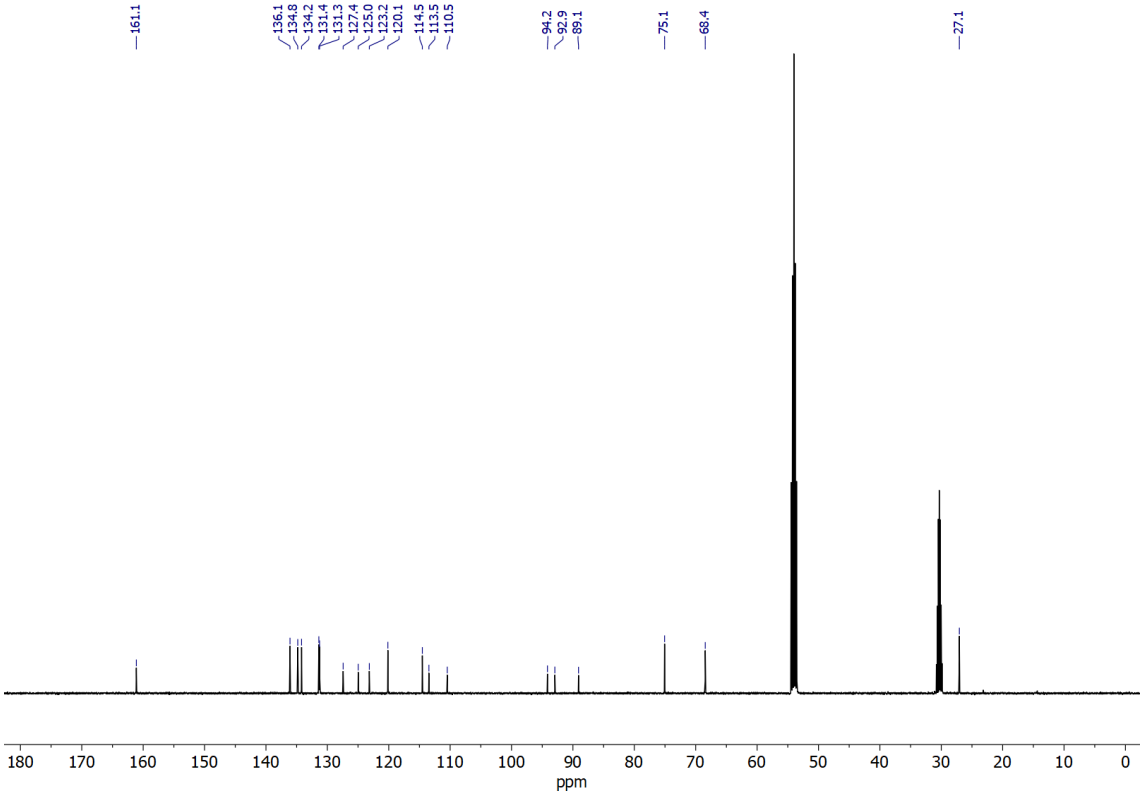


Figure S50. ^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-1:Ag(I)**.

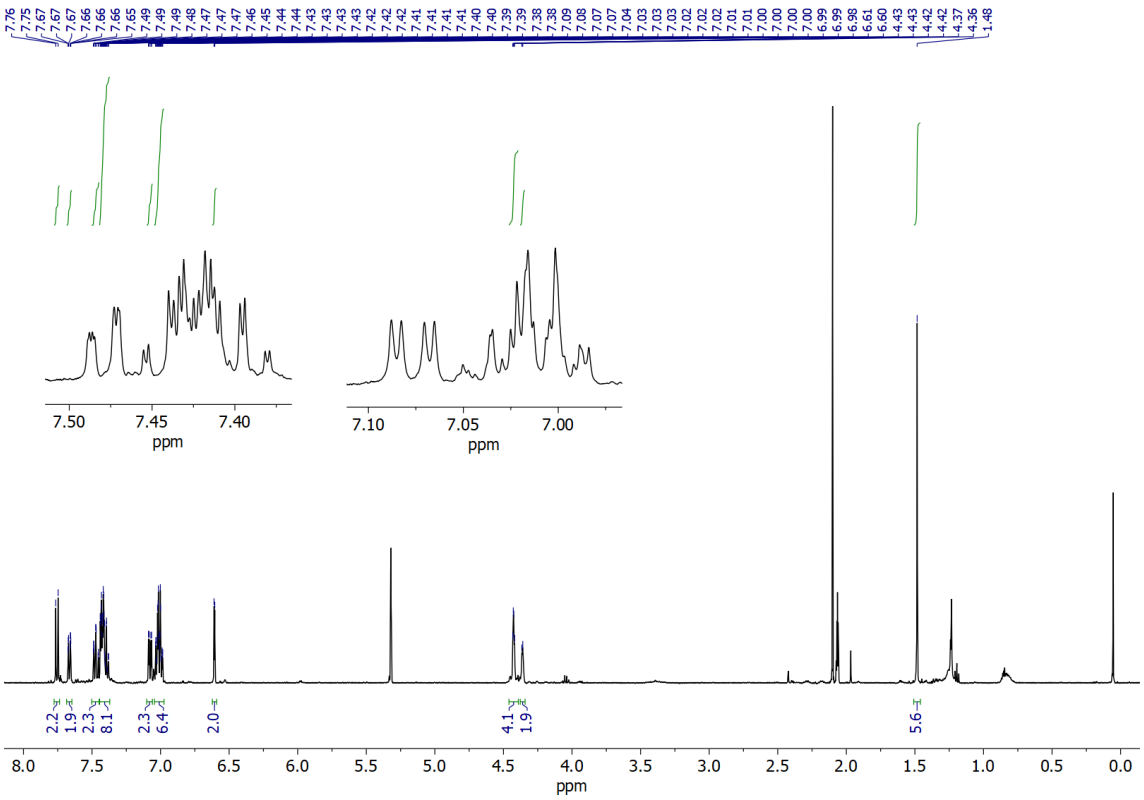


Figure S51. ^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-2:Ag(I)**.

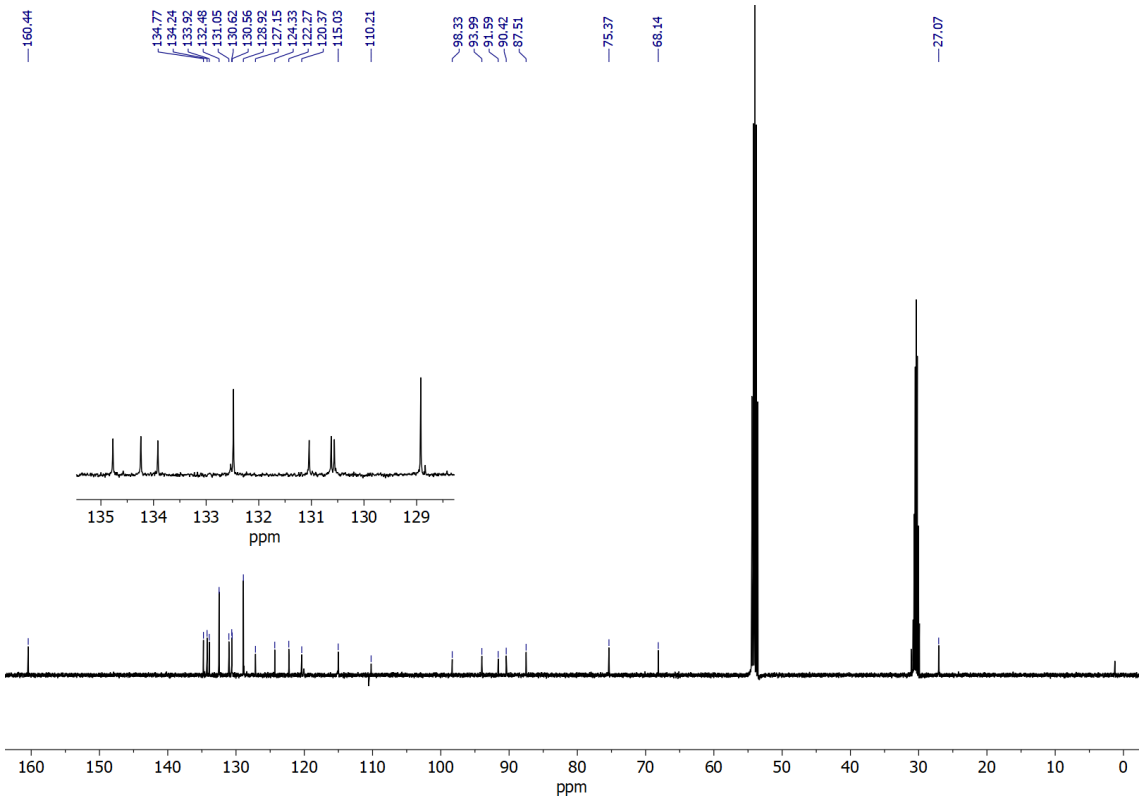


Figure S52. ^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-2:Ag(I)**.

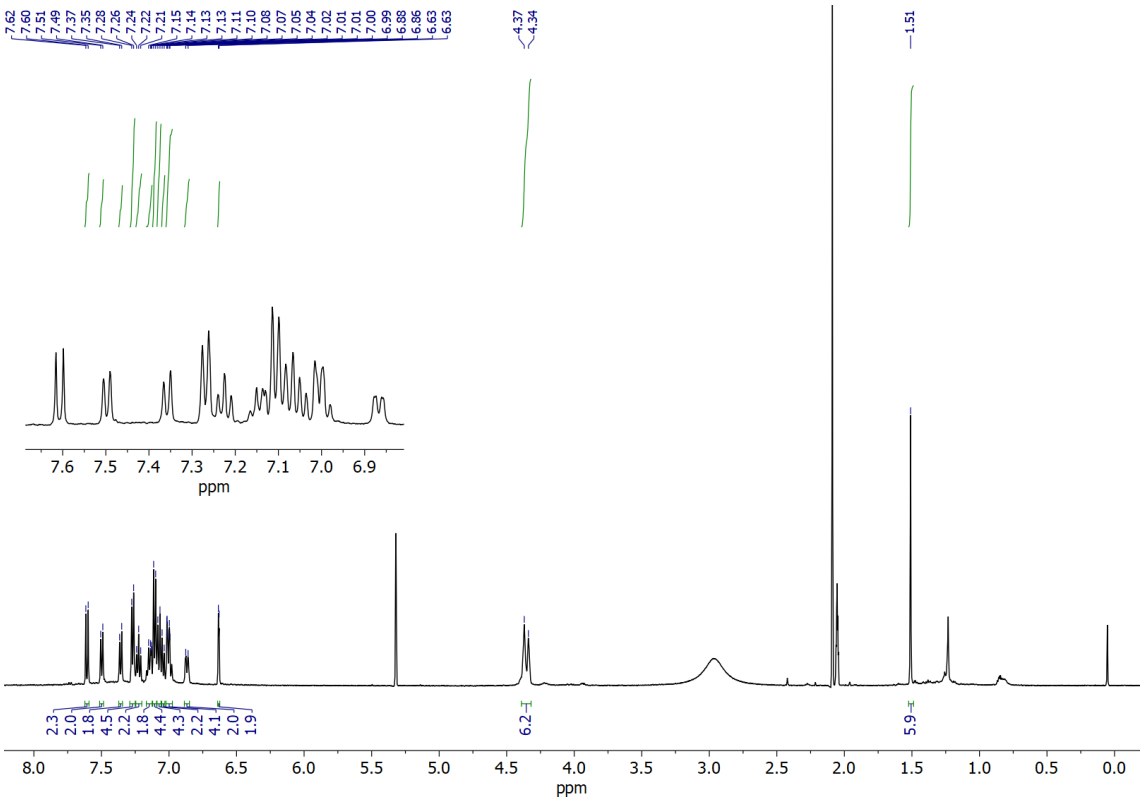


Figure S53. ^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-3:Ag(I)**.

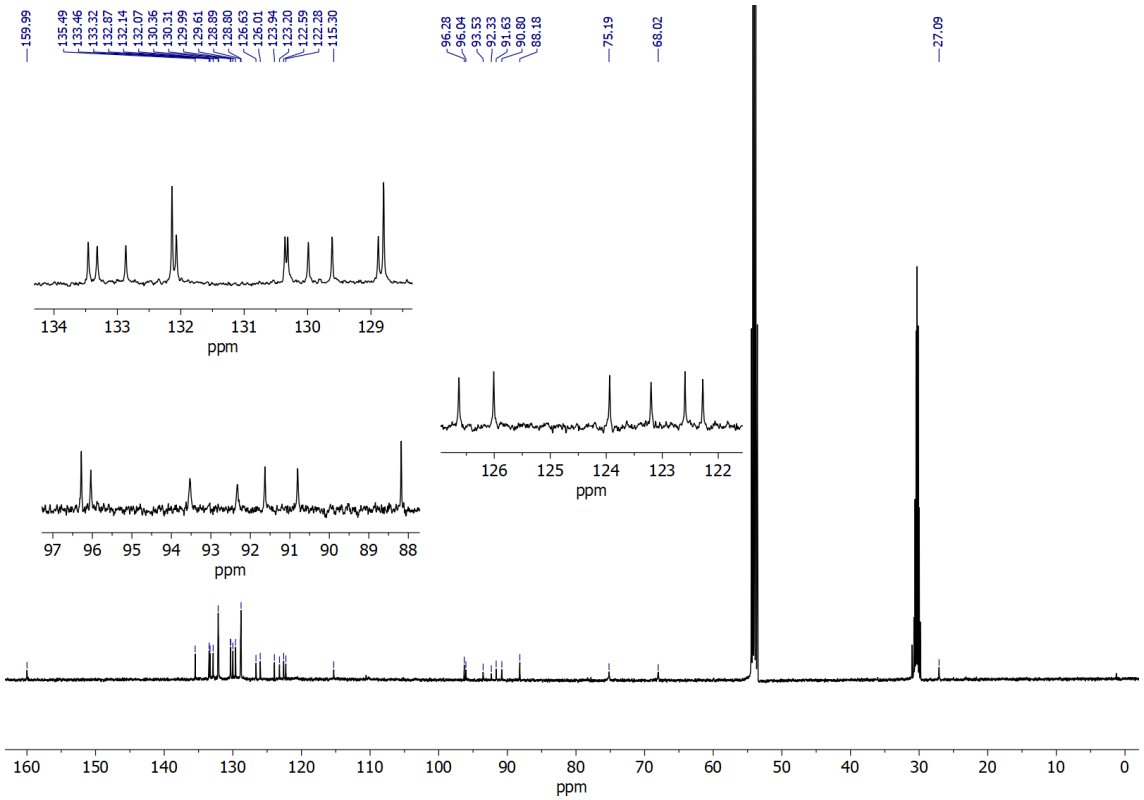


Figure S54. ^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-3:Ag(I)**.

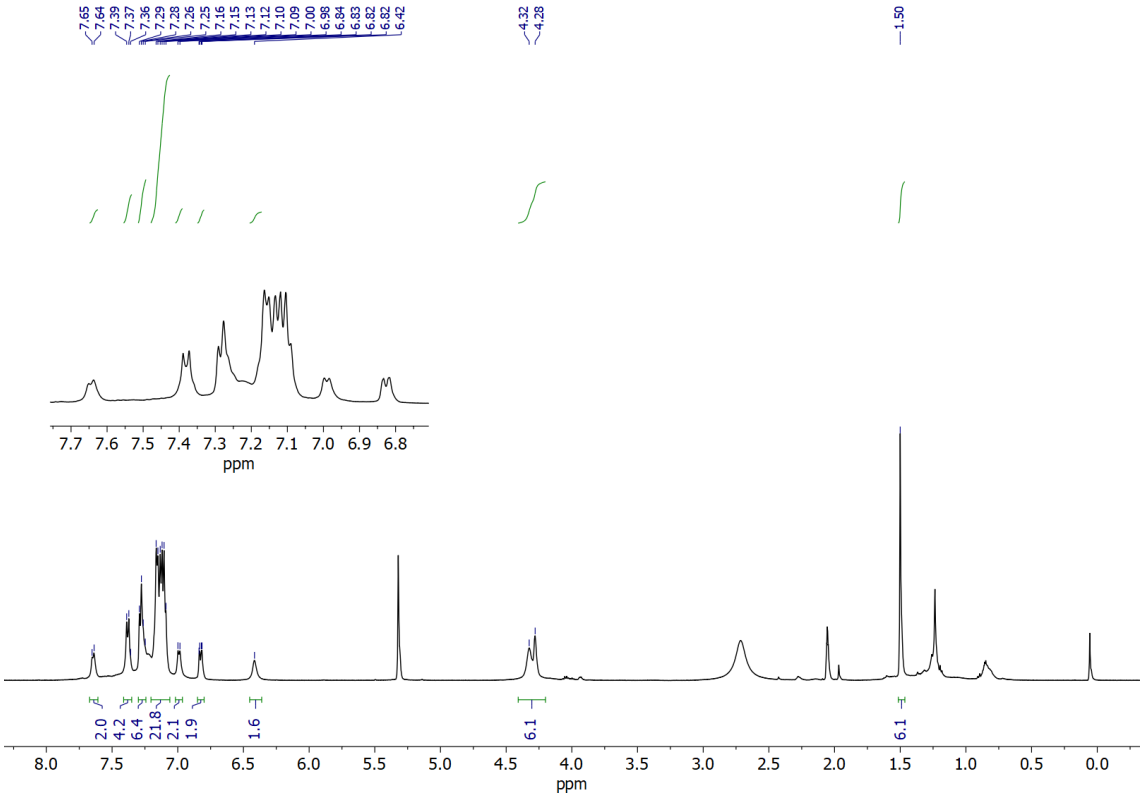


Figure S55. ^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-4:Ag(I)**.

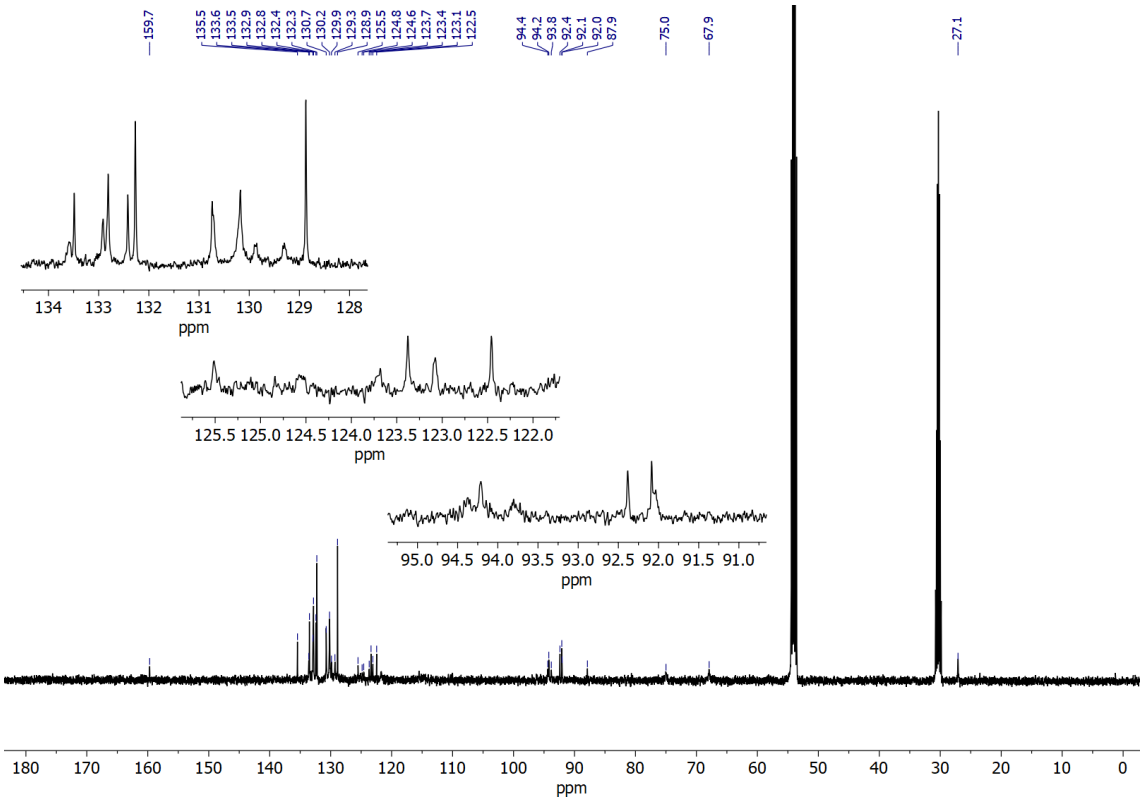


Figure S56. ^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-4:Ag(I)**.

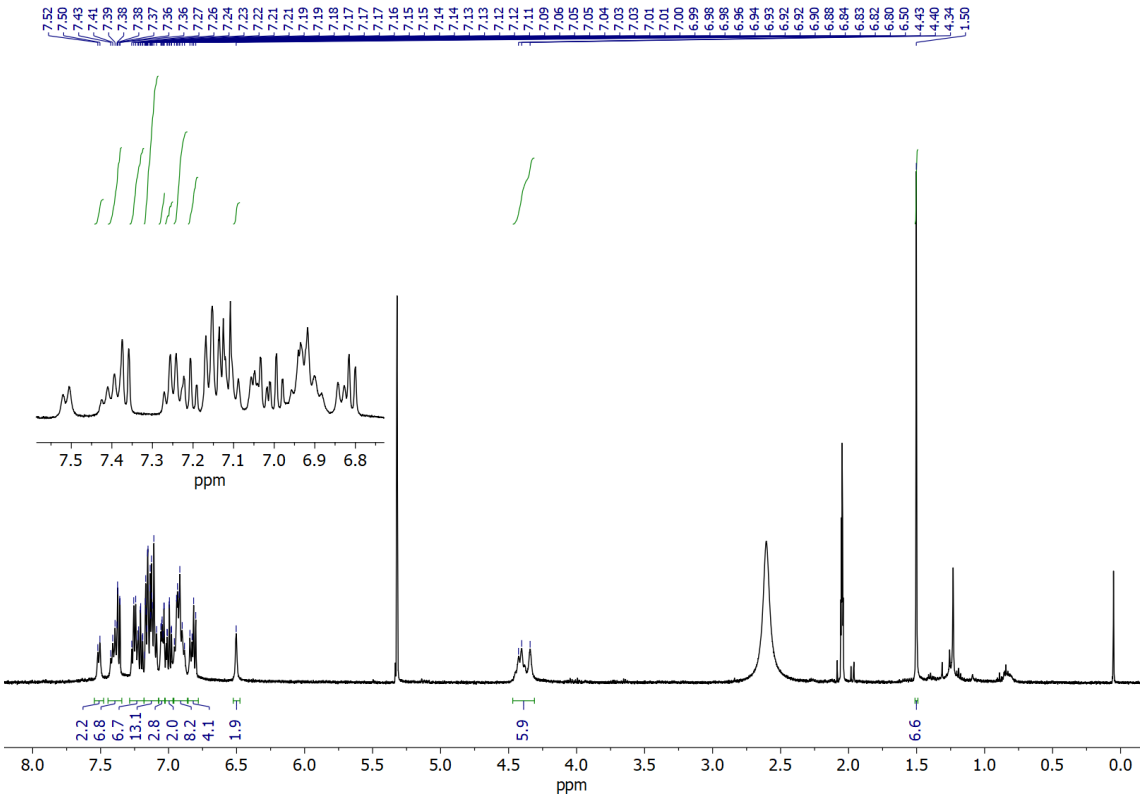


Figure S57. ^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-5:Ag(I)**.

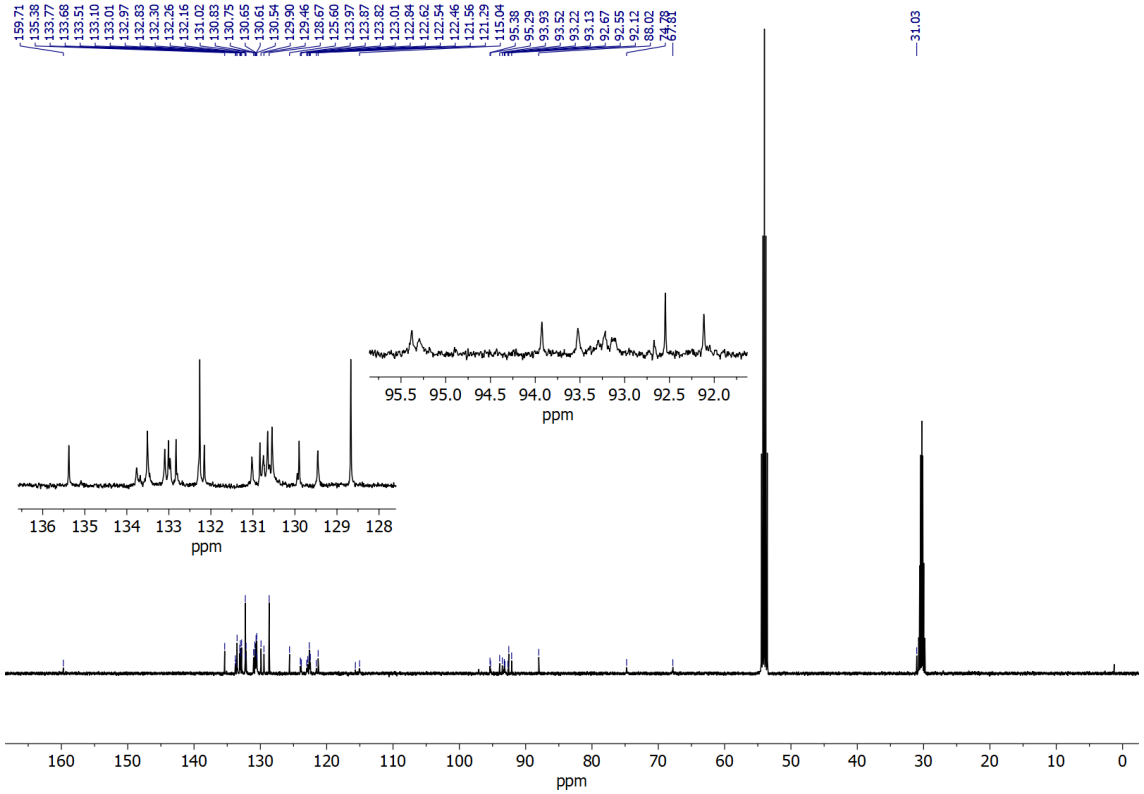


Figure S58. ^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-5:Ag(I)**.

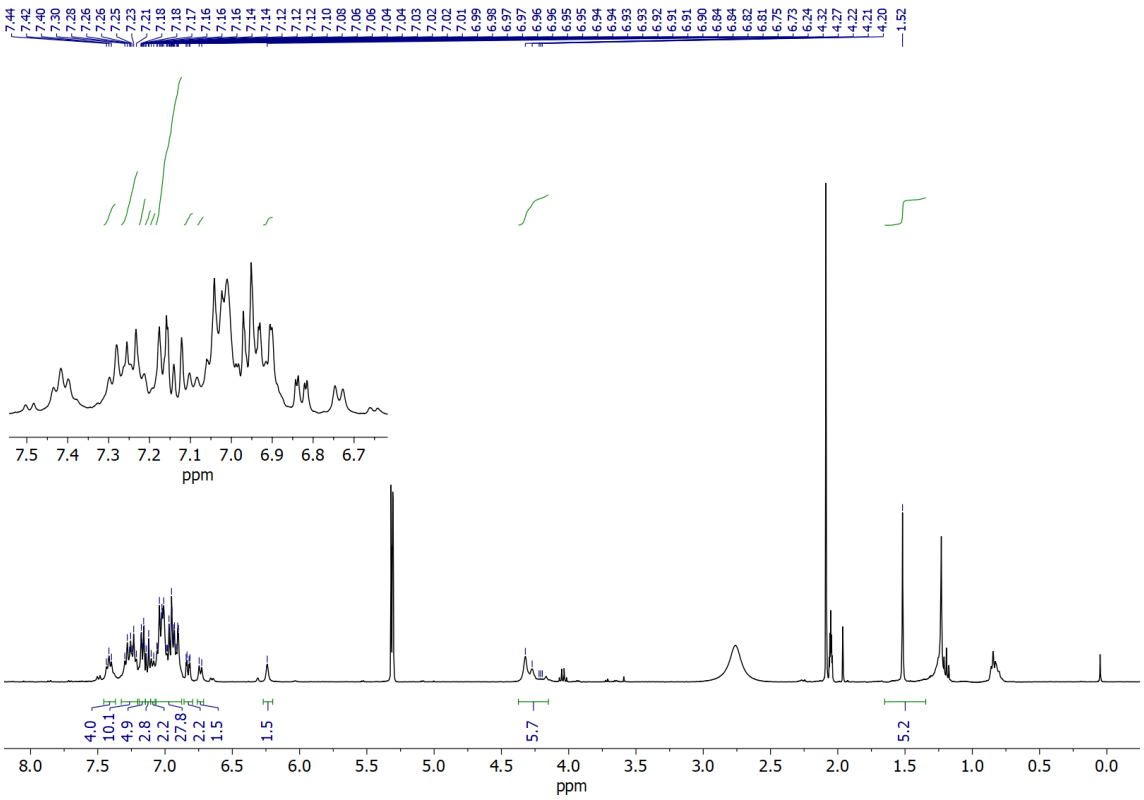


Figure S59. ^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-6:Ag(I)**.

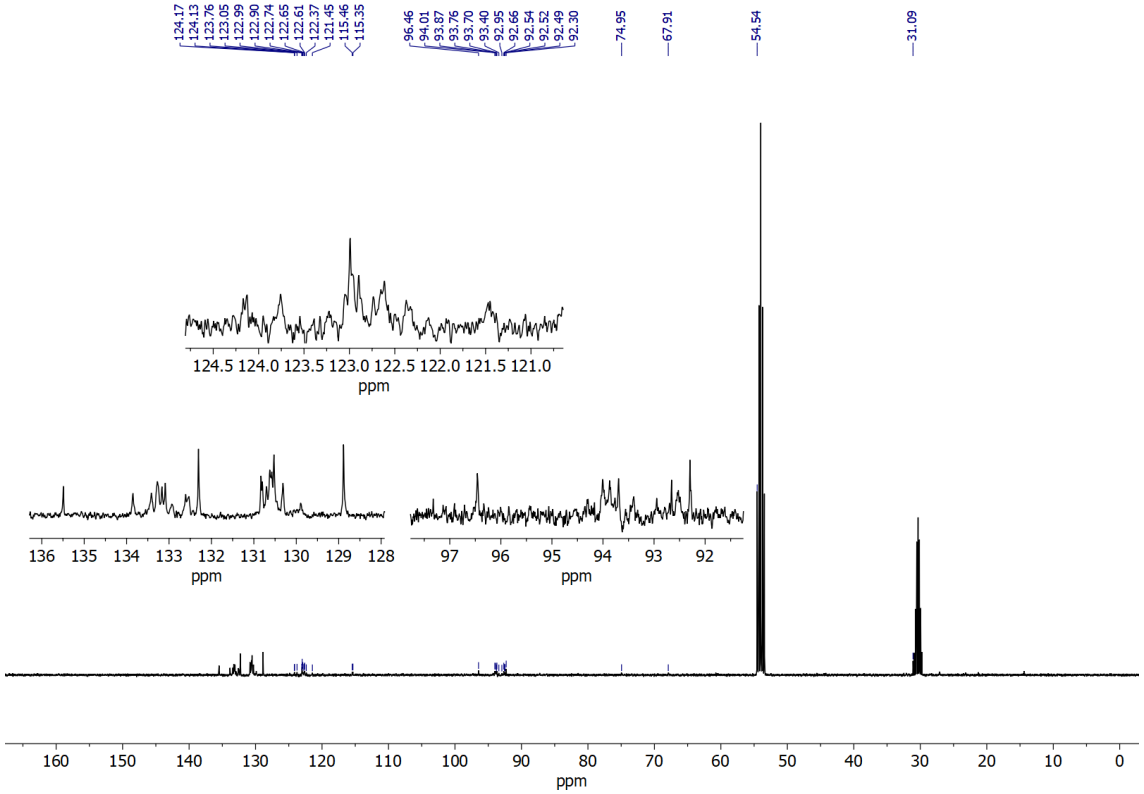


Figure S60. ^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-6:Ag(I)**.

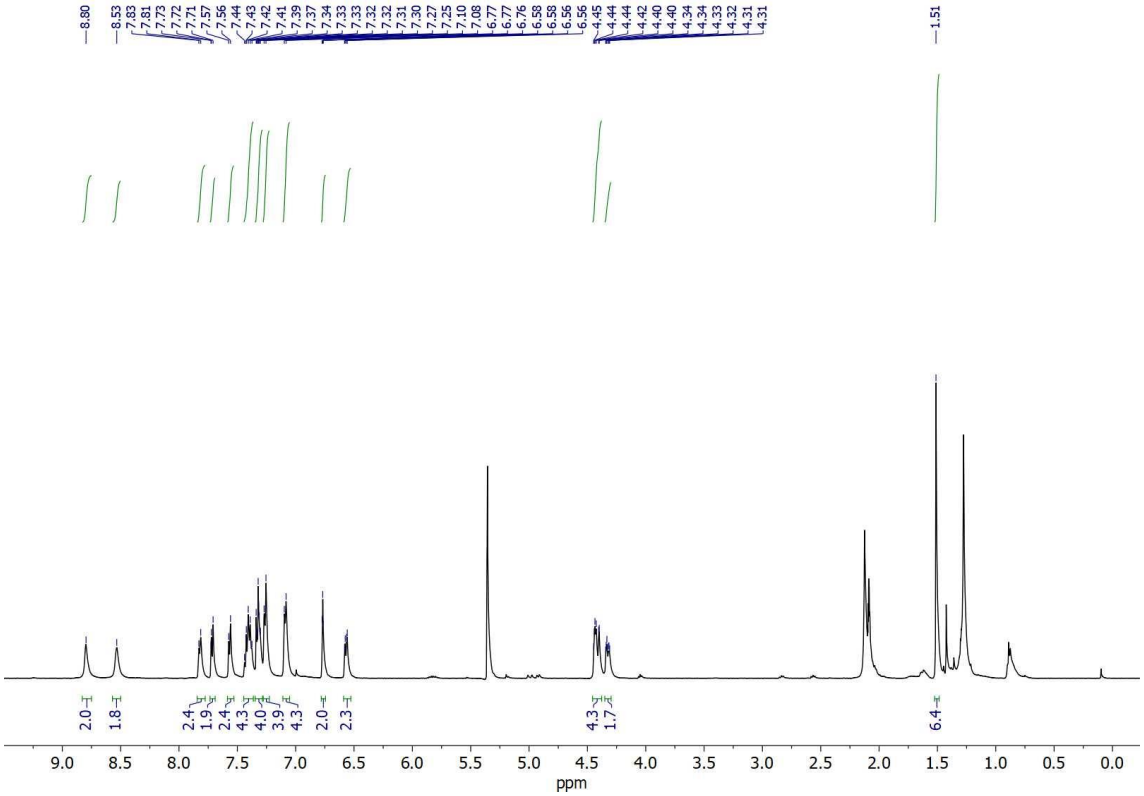


Figure S61. ^{1}H NMR (500 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-7:Ag(I)**.

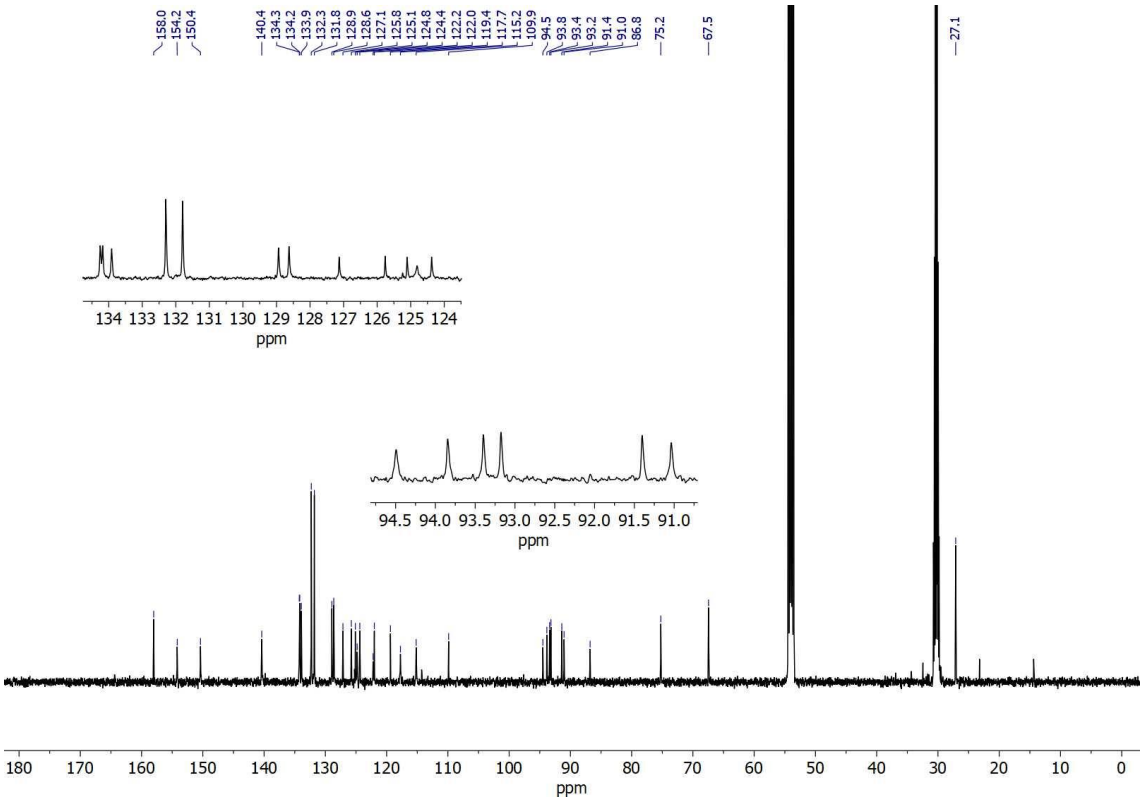


Figure S62. ^{13}C NMR (126 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectrum of **(*S,S,P*)-7:Ag(I)**.

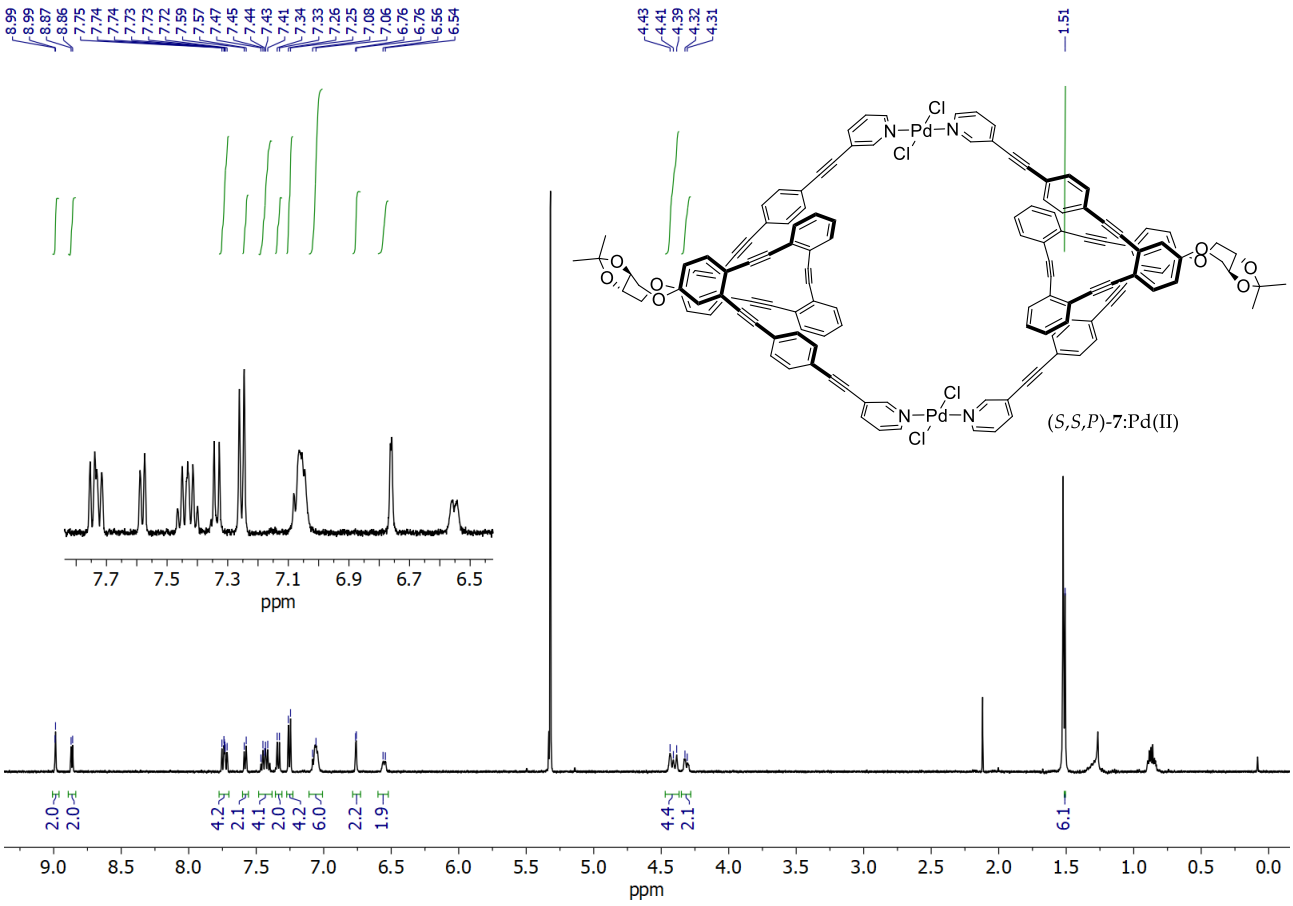


Figure S63. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of ((*S,S,P*)-**7**)$_2$Pd$_2$.

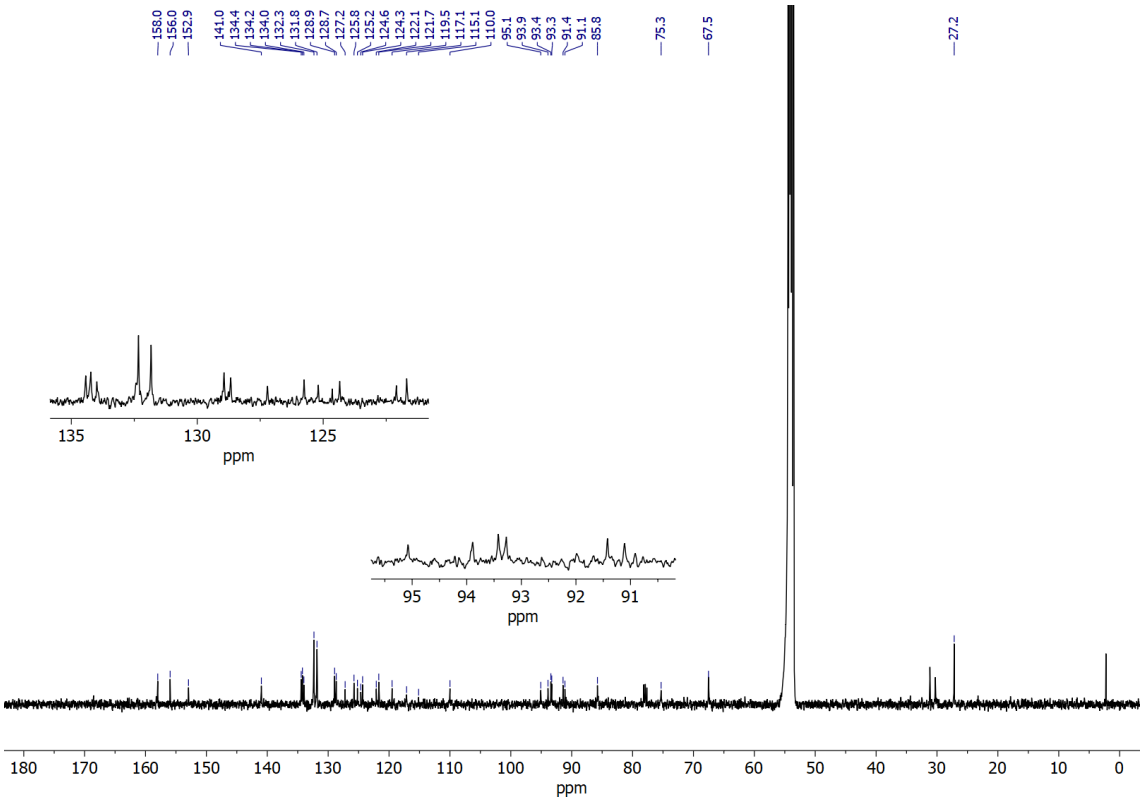


Figure S64. ^{13}C NMR (126 MHz, CD_2Cl_2) spectrum of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

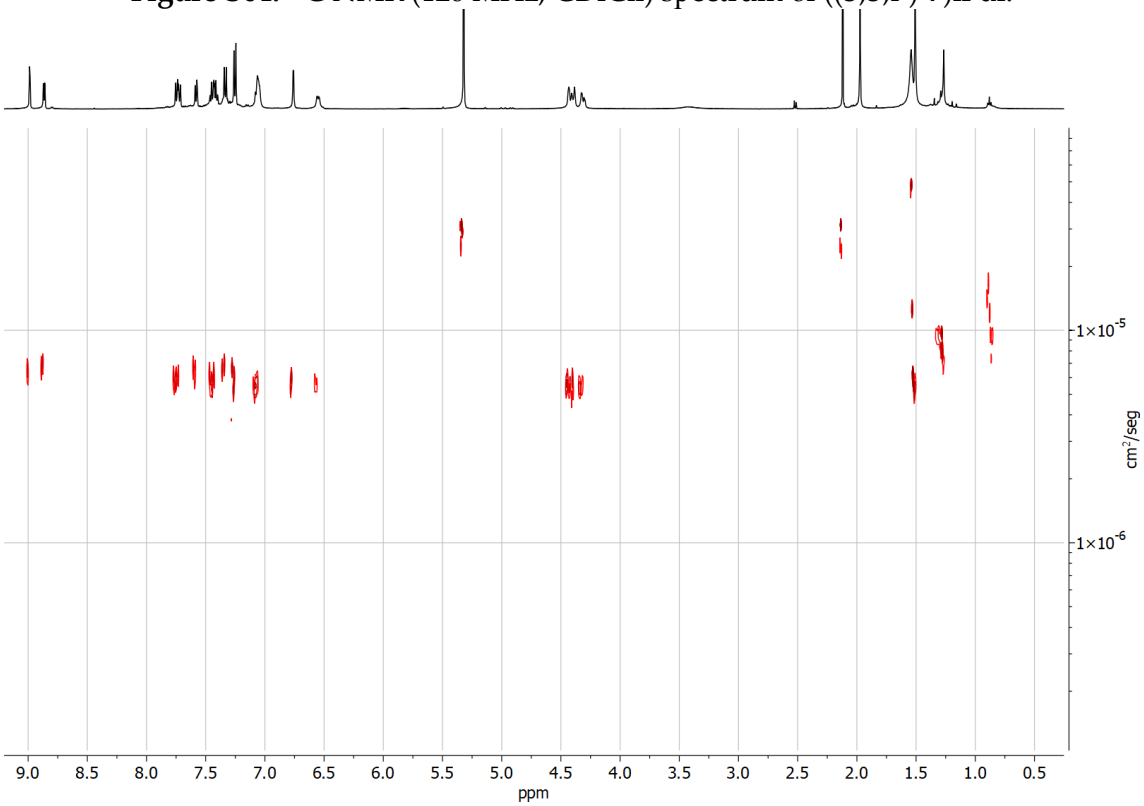


Figure S65. DOSY NMR (500 MHz, CD_2Cl_2) spectrum of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

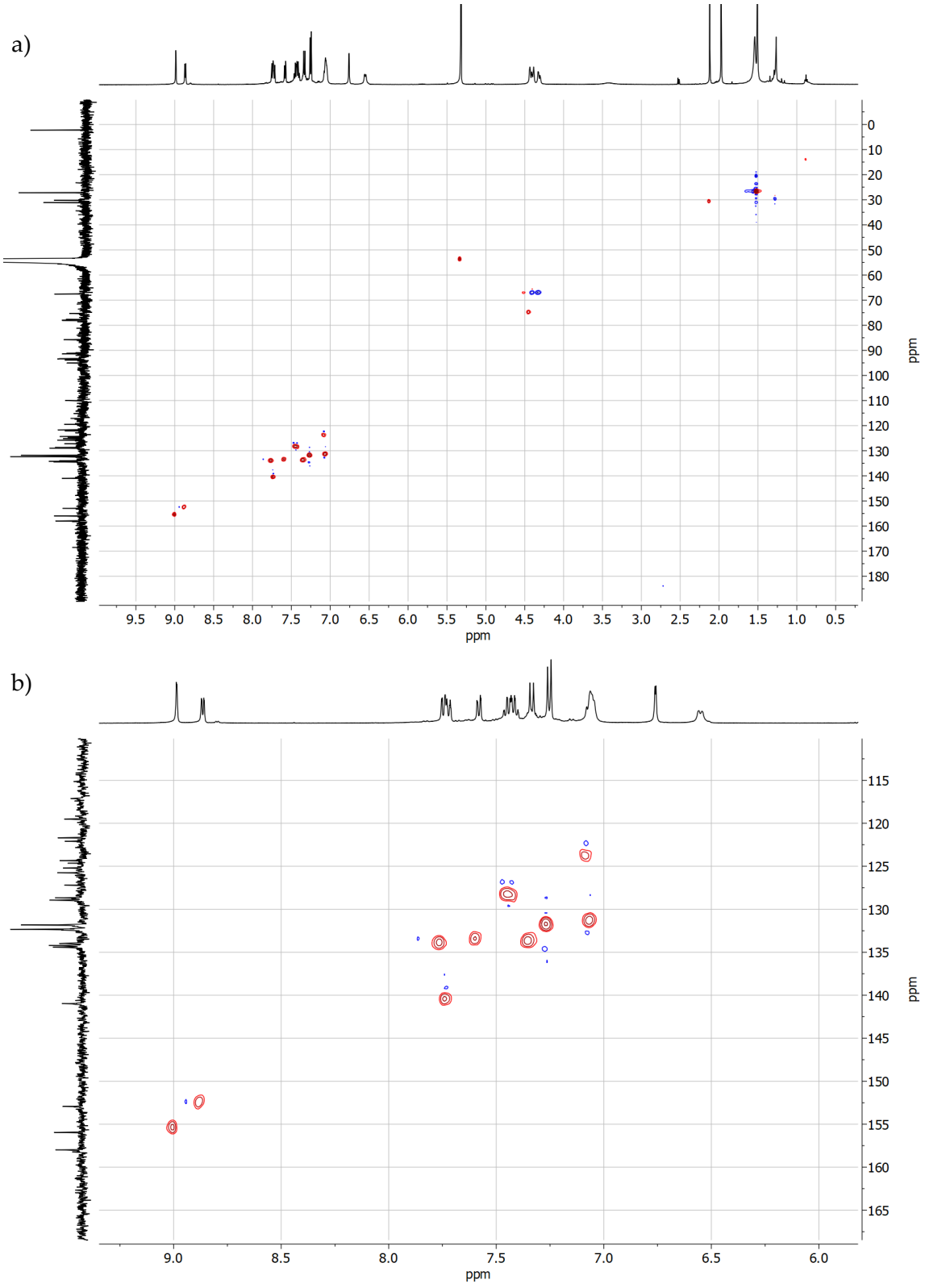


Figure S66. a) Complete and **b)** partial HSQC NMR (500 MHz and 126 MHz, CD_2Cl_2) spectrum of ((*S*,*S*,*P*)-**7**)$_2Pd_2$.

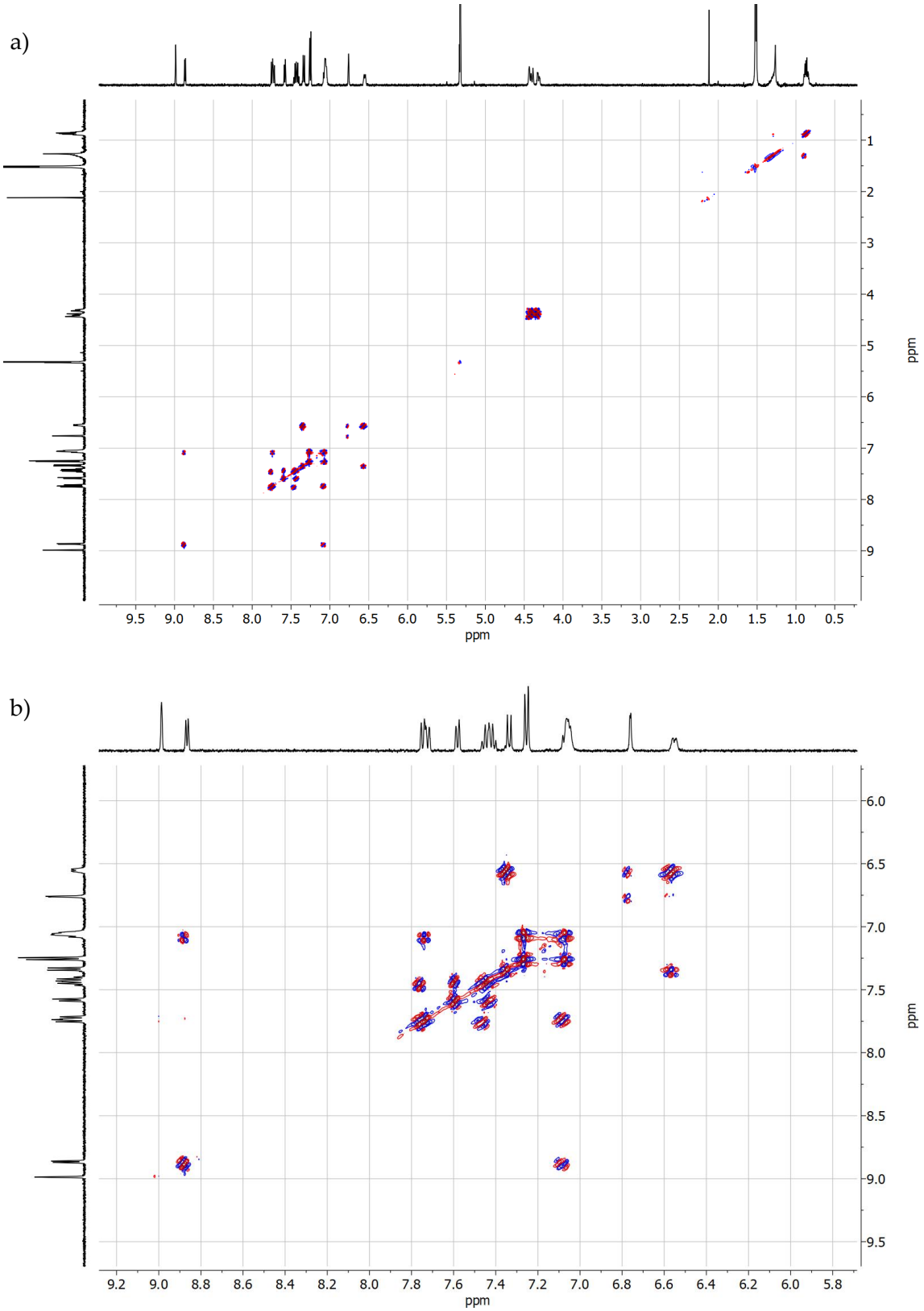


Figure S67. a) Complete and **b)** partial COSY NMR (500 MHz, CD_2Cl_2) spectrum of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

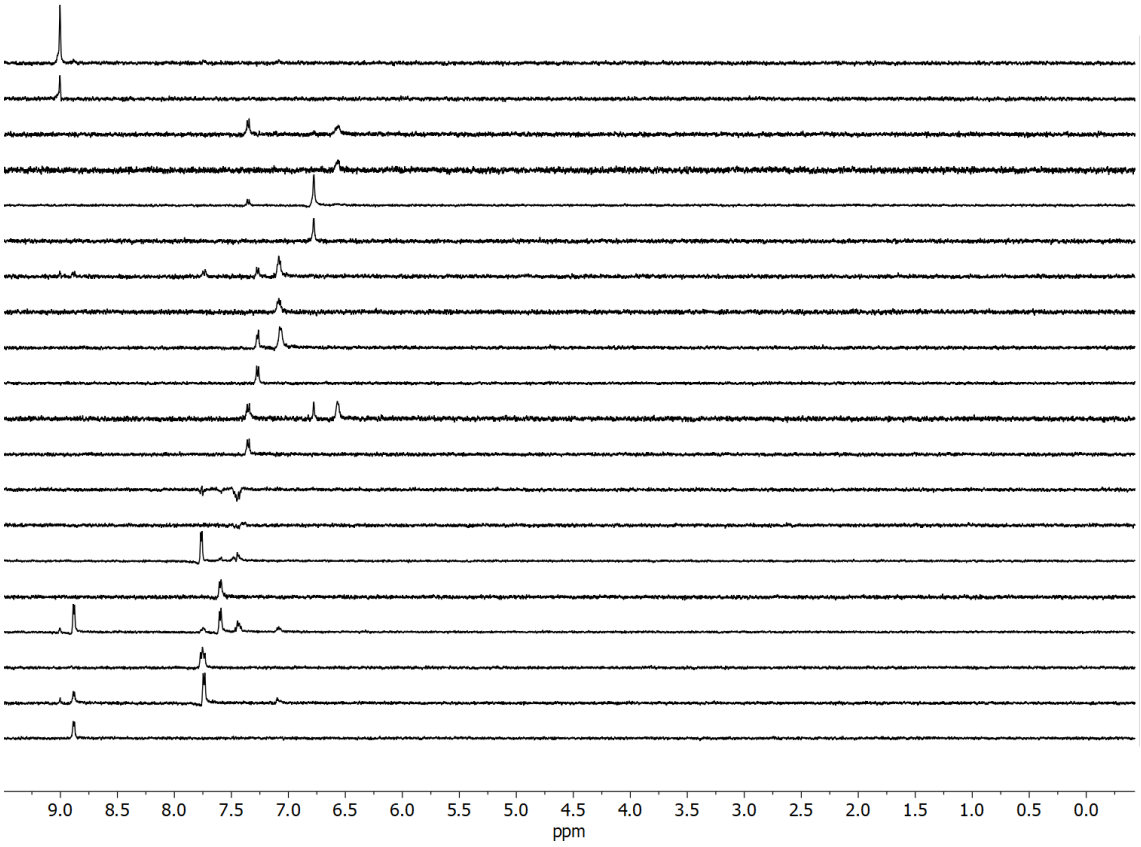


Figure S68. TOCSY NMR (500 MHz, CD_2Cl_2) spectrum of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

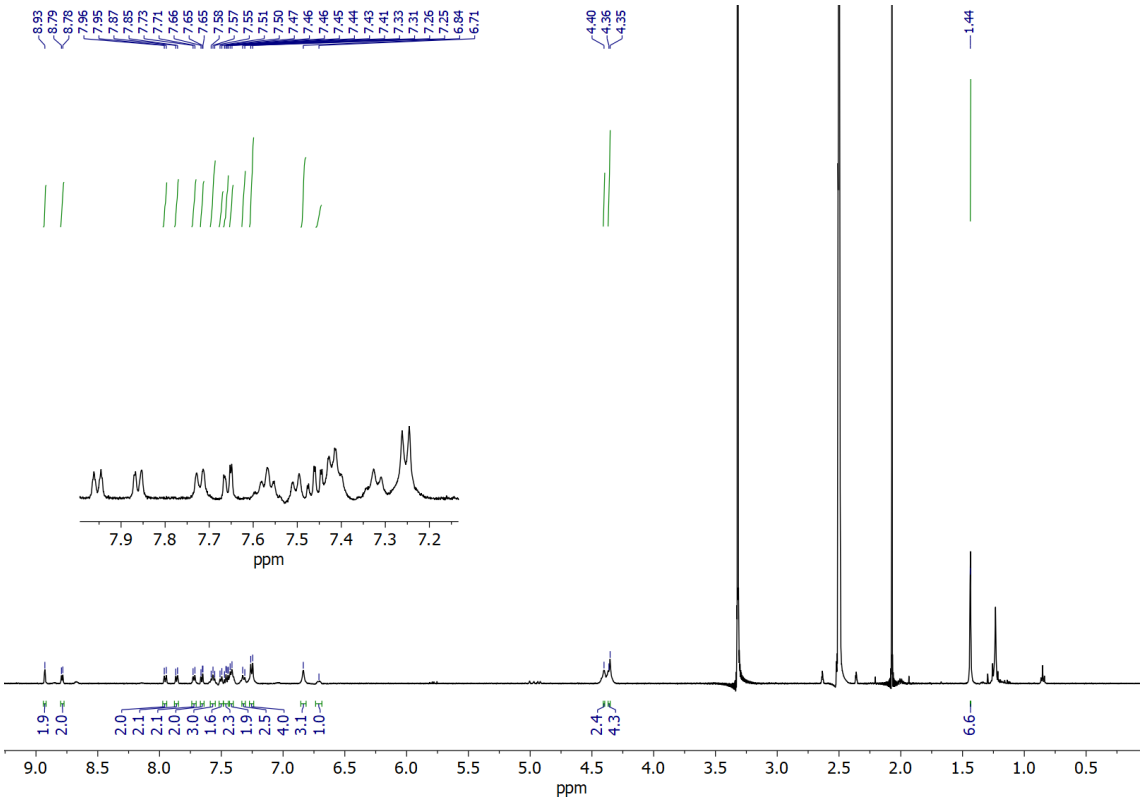


Figure S69. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

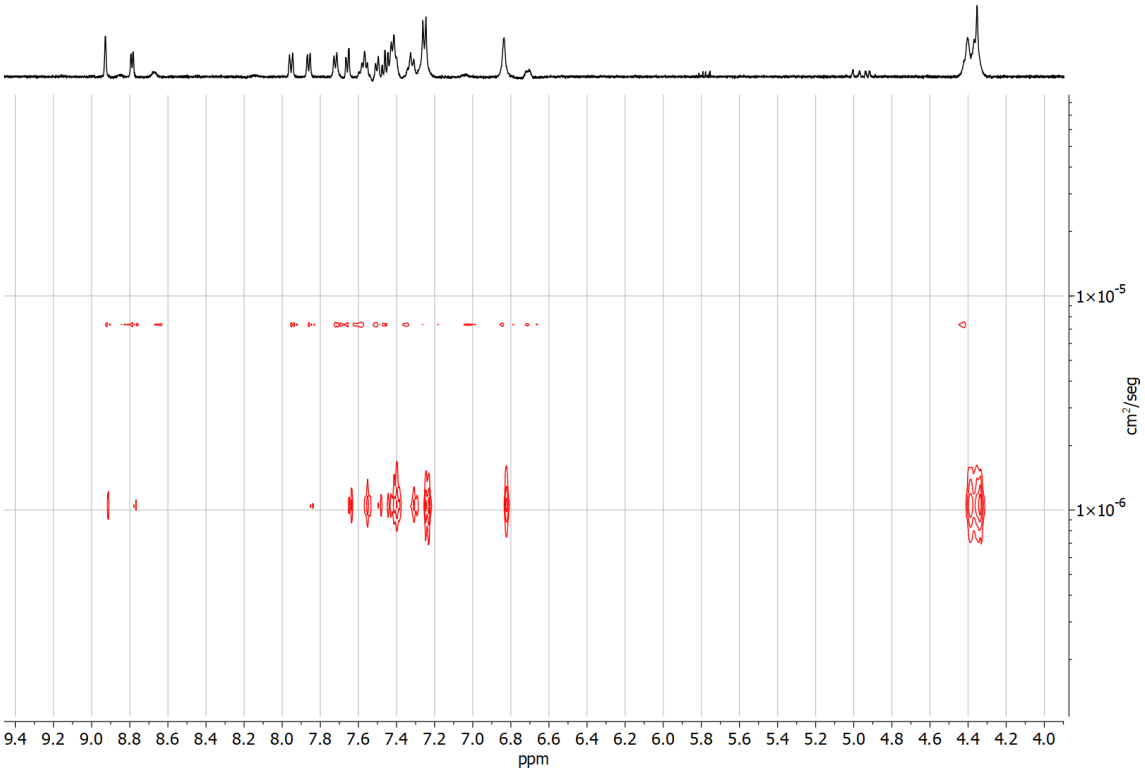


Figure S70. DOSY NMR (500 MHz, DMSO-d_6) spectrum of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

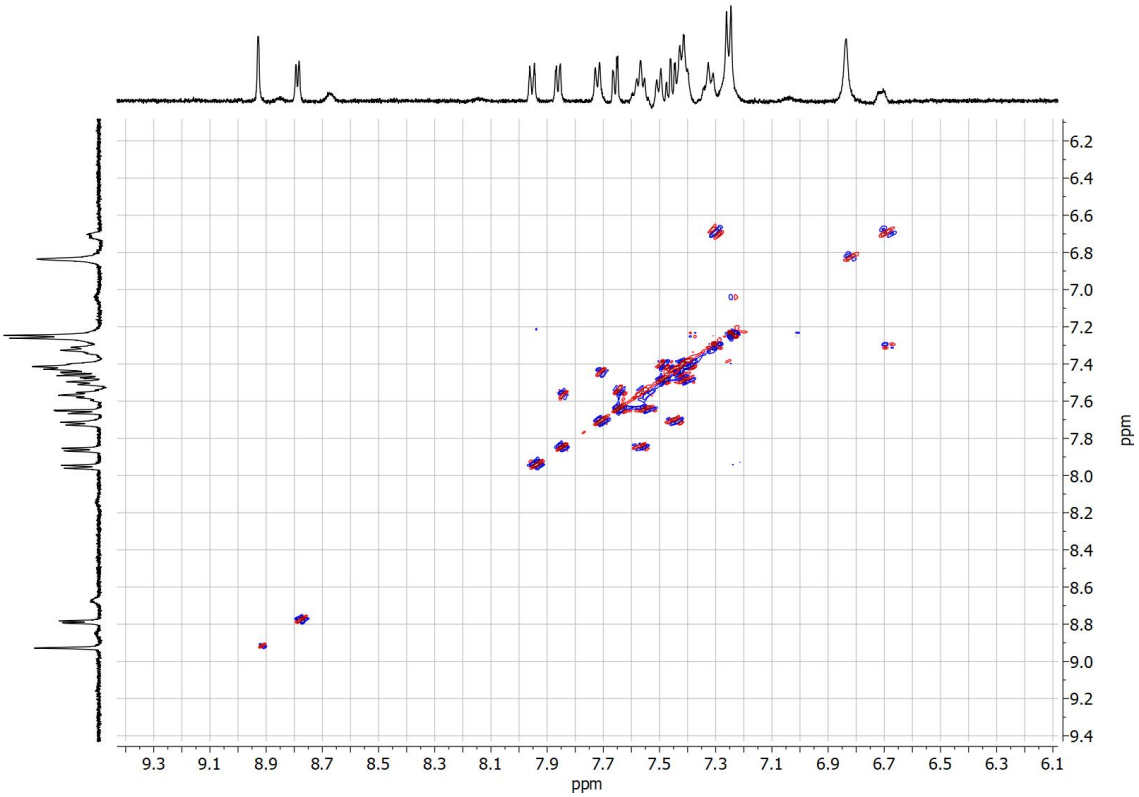


Figure S71. COSY NMR (500 MHz, DMSO-d_6) spectrum of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

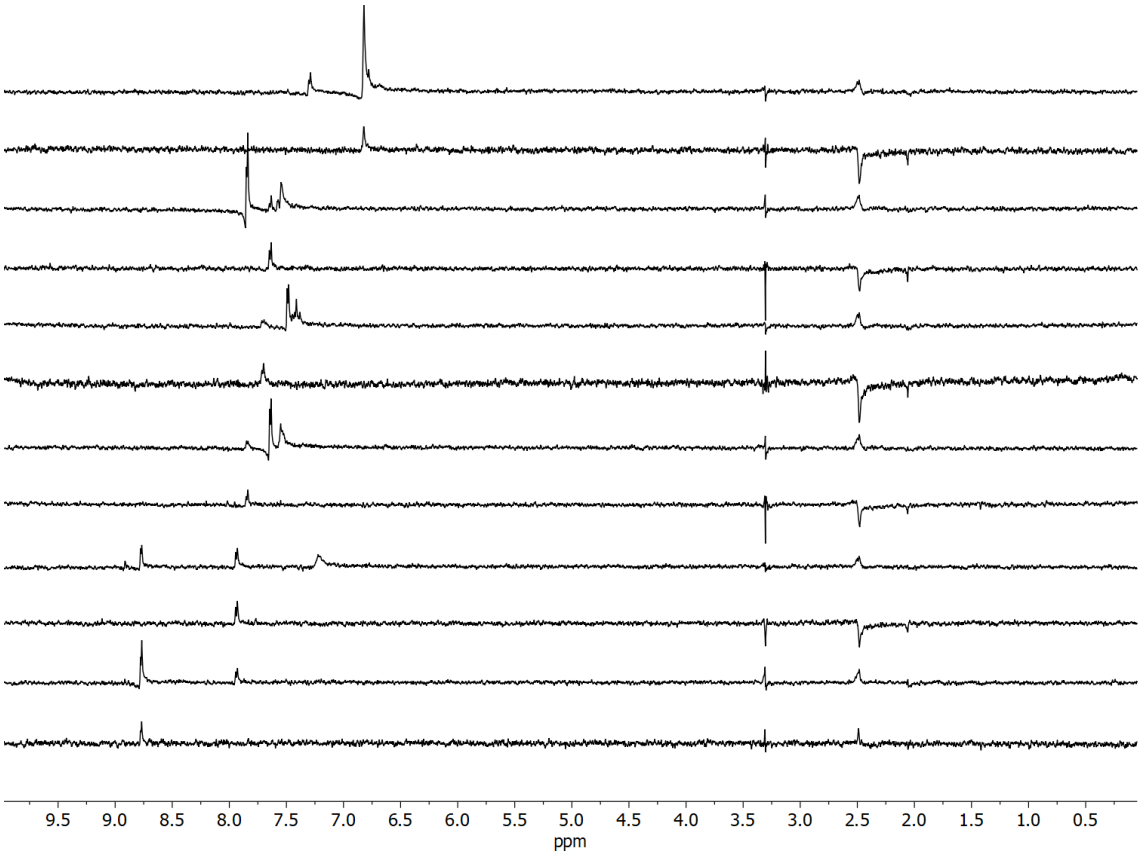


Figure S72. TOCSY NMR (500 MHz, DMSO-d_6) spectrum of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

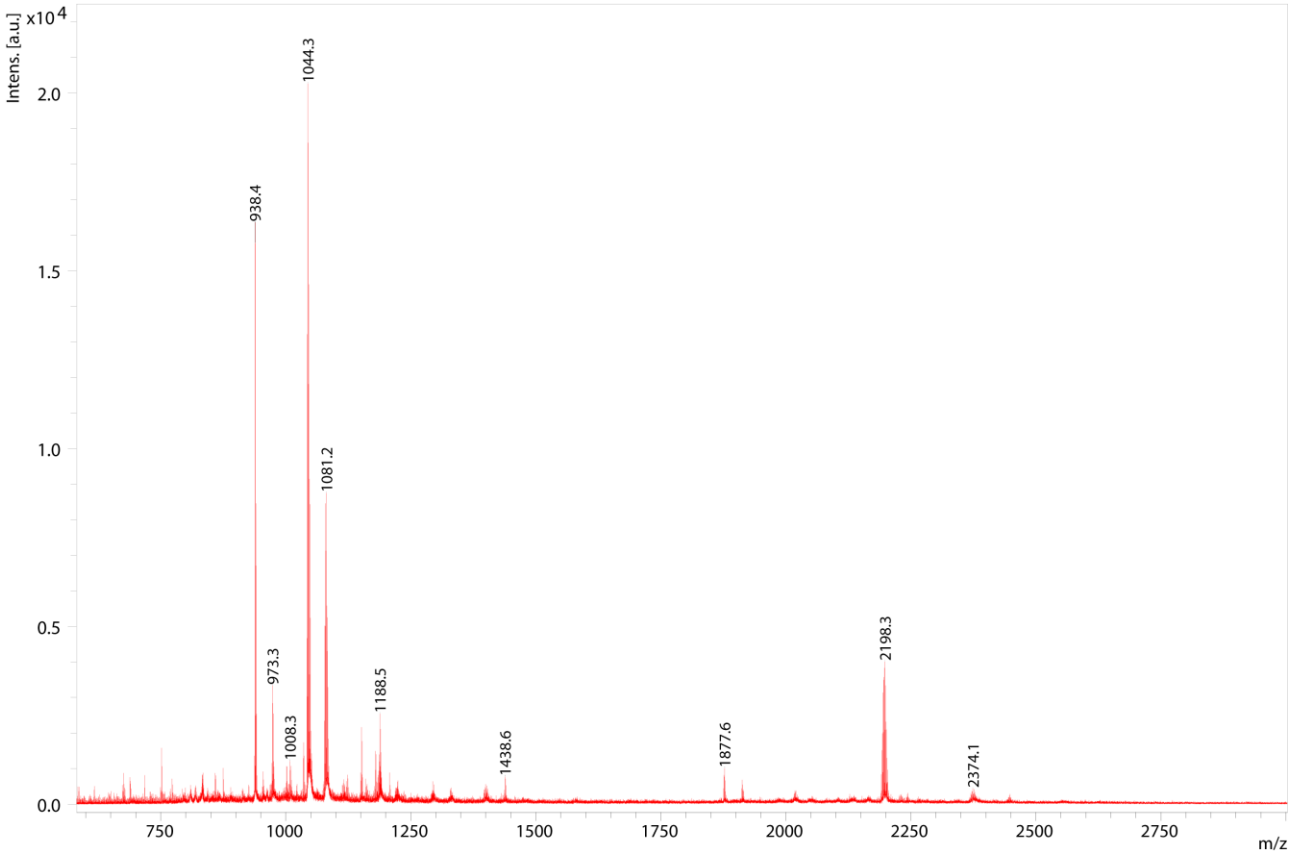


Figure S73. Full range mass spectrum of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

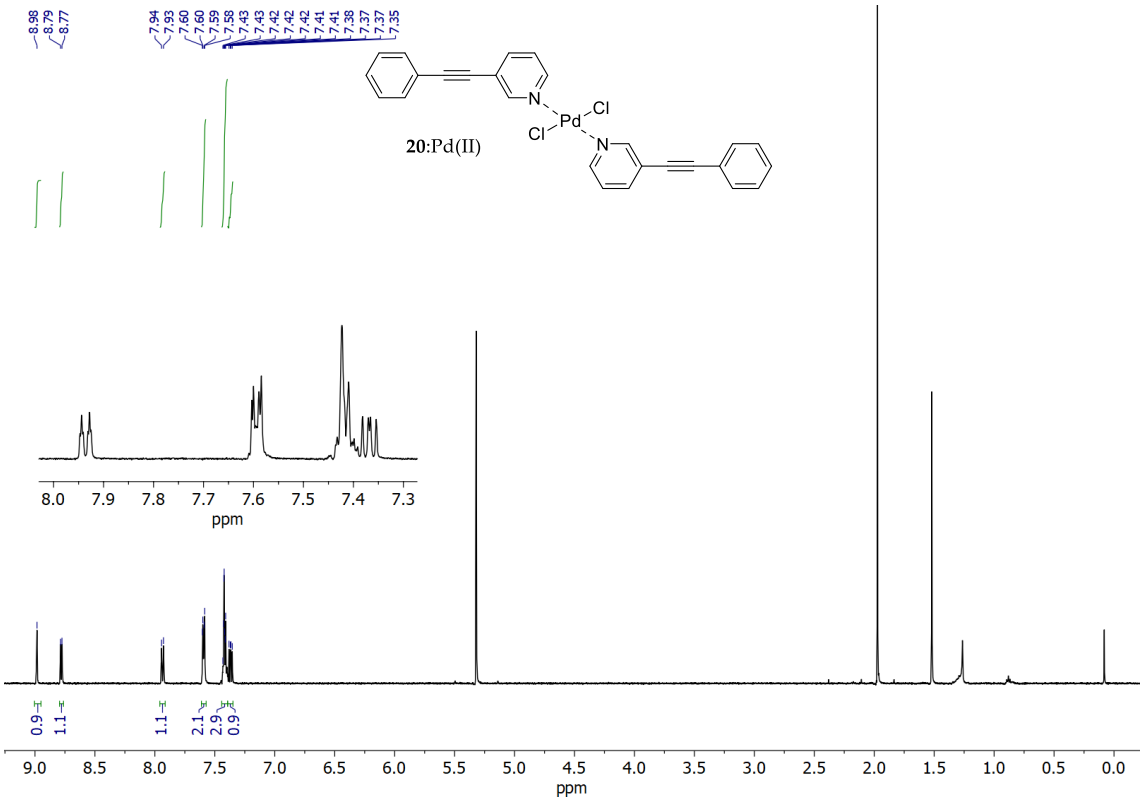


Figure S74. ^{1}H NMR (500 MHz, CD_2Cl_2) spectrum of (**20**)$_2$Pd.

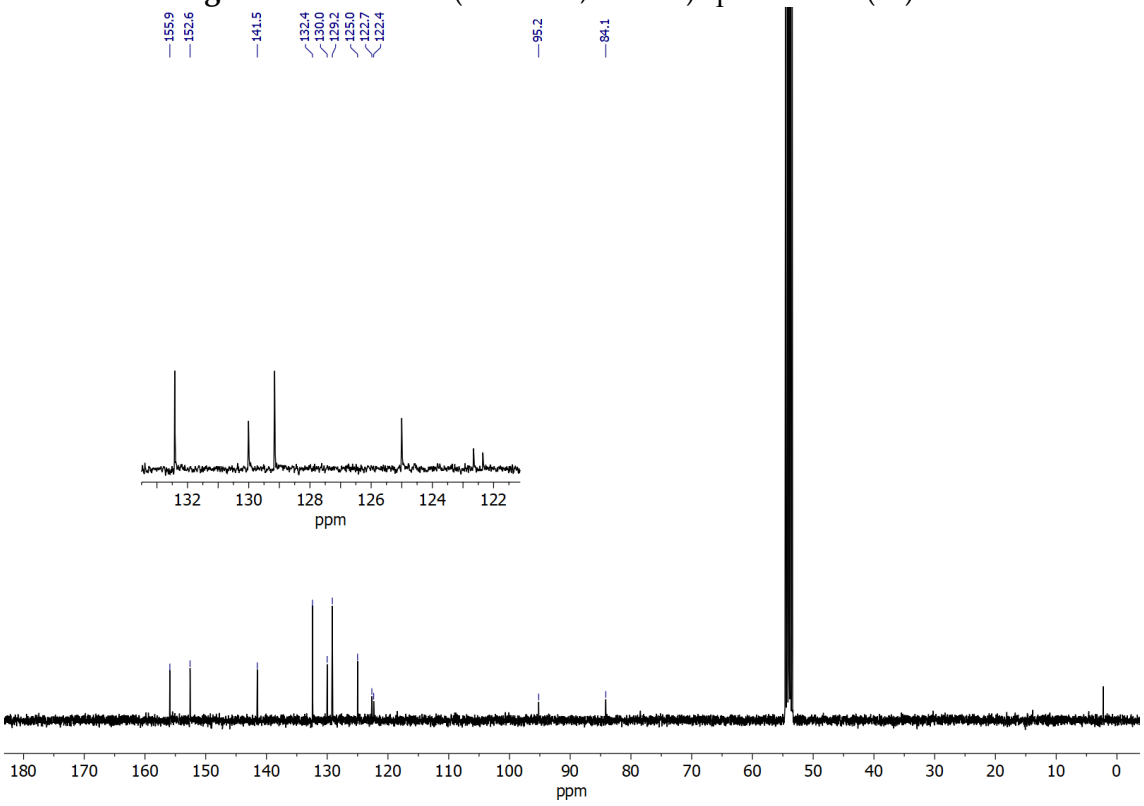


Figure S75. ^{13}C NMR (126 MHz, CD_2Cl_2) spectrum of (**20**)$_2$Pd.

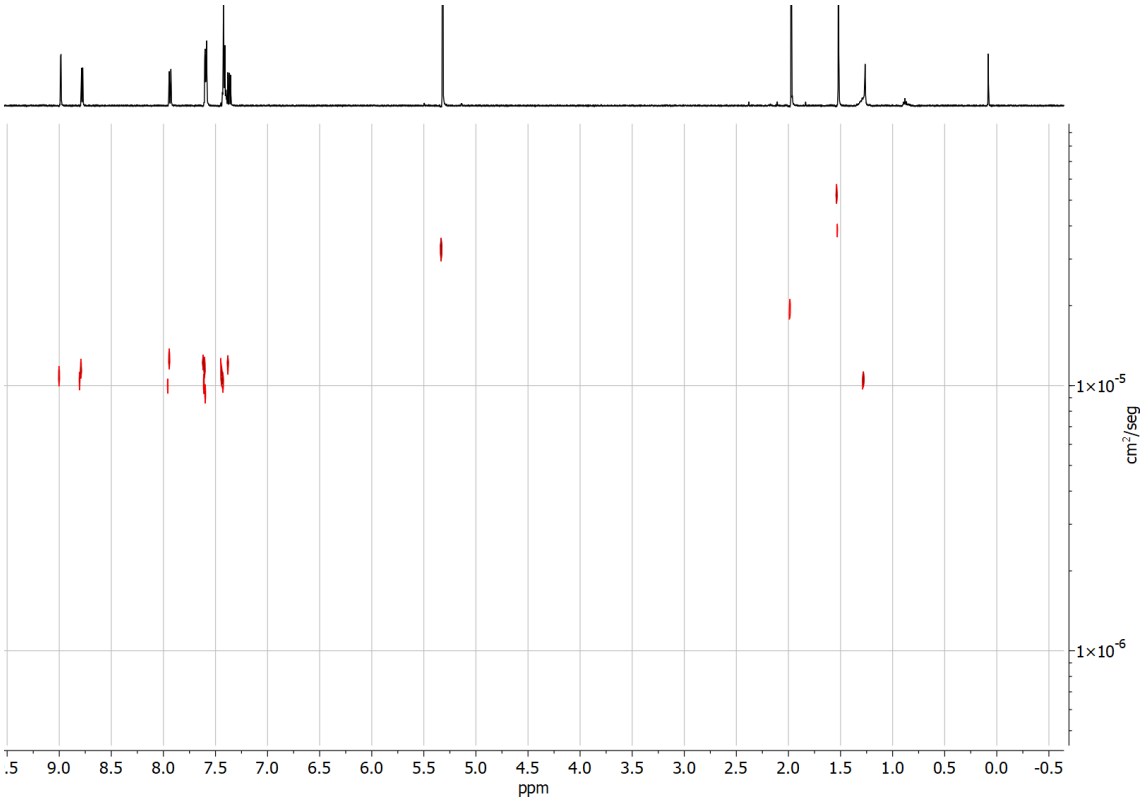


Figure S76. DOSY NMR (500 MHz, CD_2Cl_2) spectrum of (**20**)$_2$Pd.

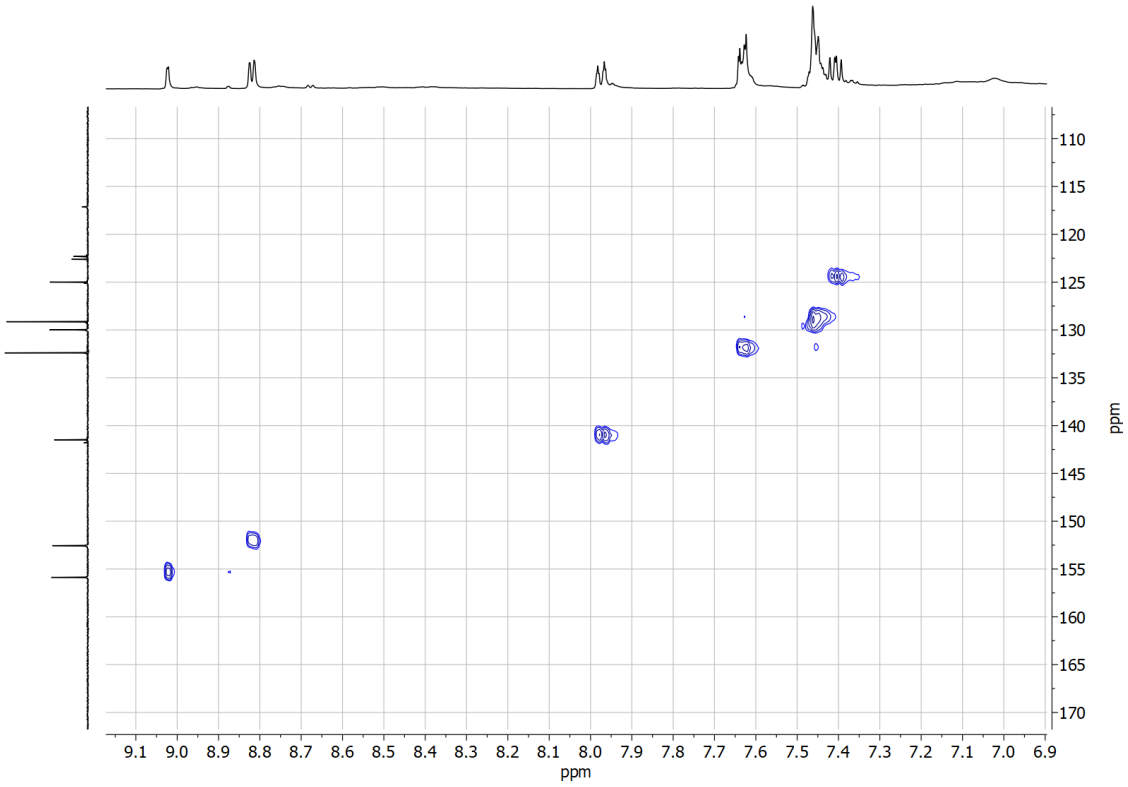


Figure S77. HSQC NMR (500 MHz and 126 MHz, CD_2Cl_2) spectrum of (**20**)$_2$Pd.

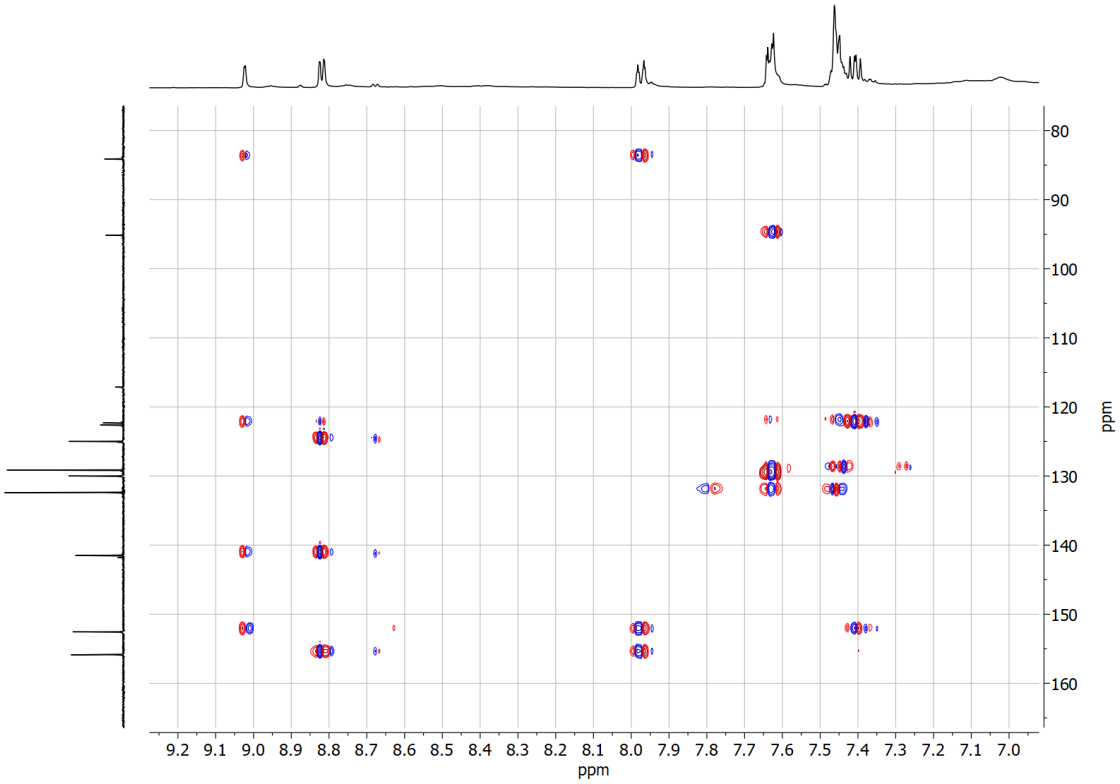


Figure S78. HMBC NMR (500 MHz and 126 MHz, CD_2Cl_2) spectrum of (**20**)$_2$Pd.

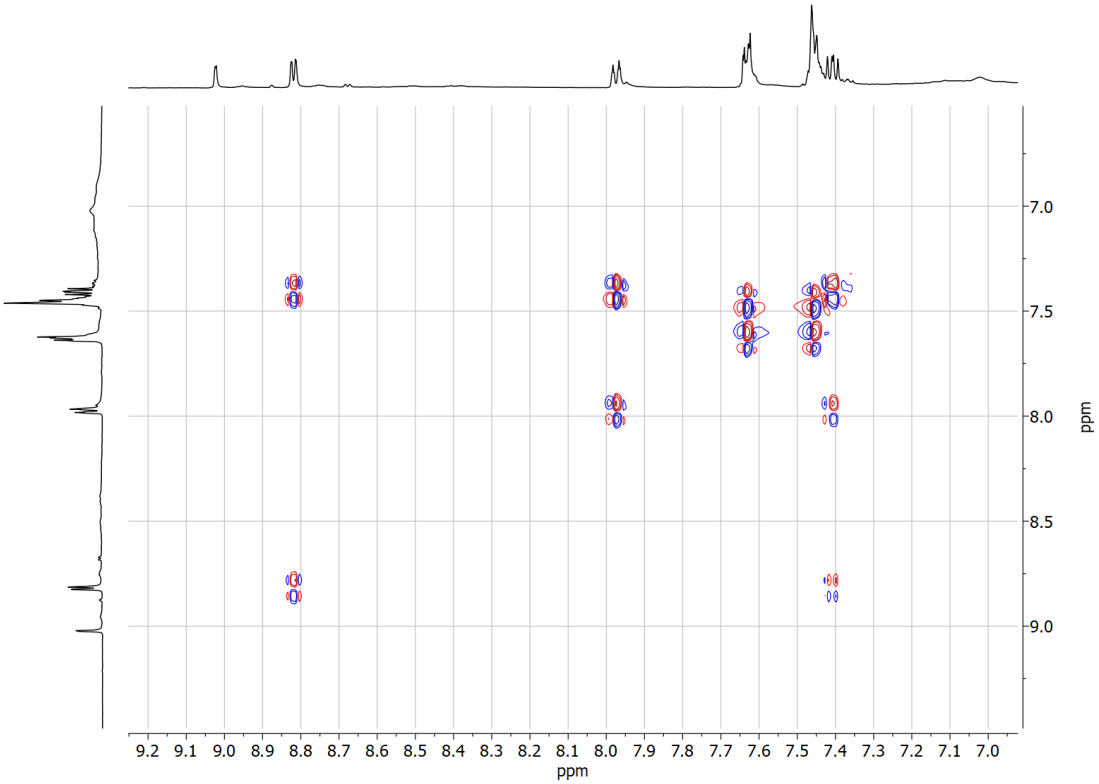


Figure S79. COSY NMR (500 MHz, CD_2Cl_2) spectrum of (**20**)$_2$Pd.

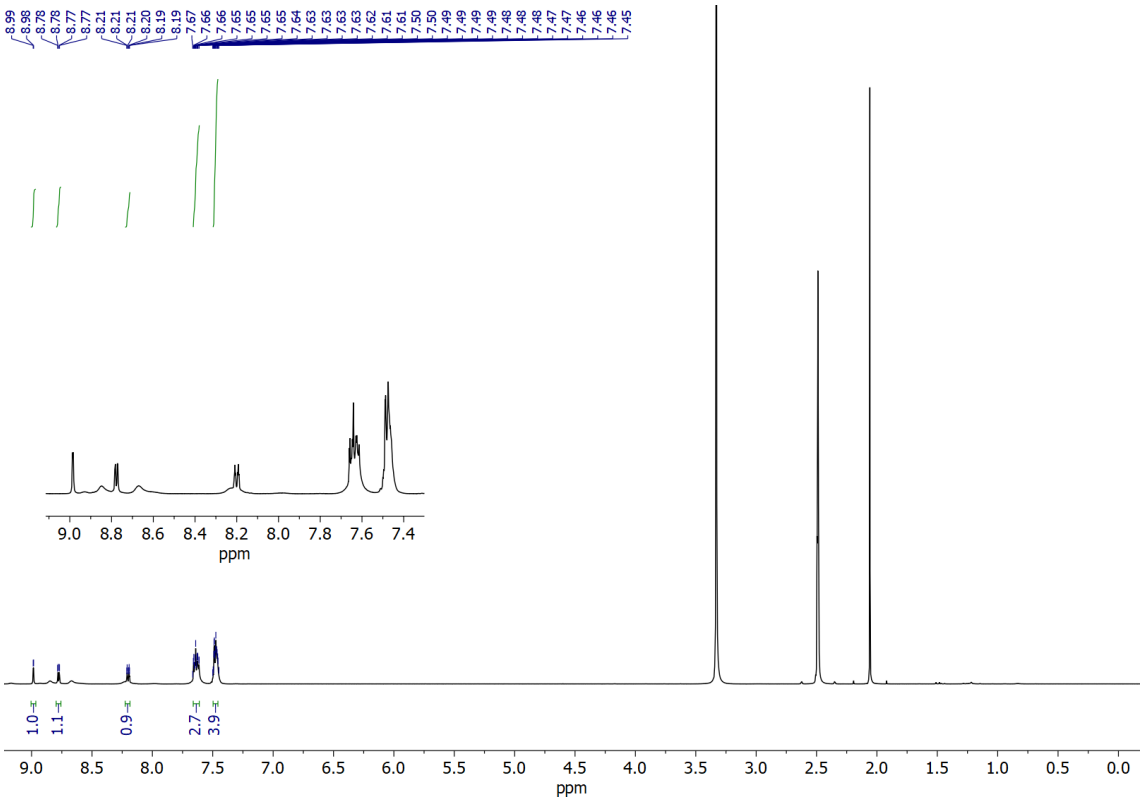


Figure S80. ^{1}H NMR (500 MHz, DMSO-d_6) spectrum of (**20**)$_2$Pd.

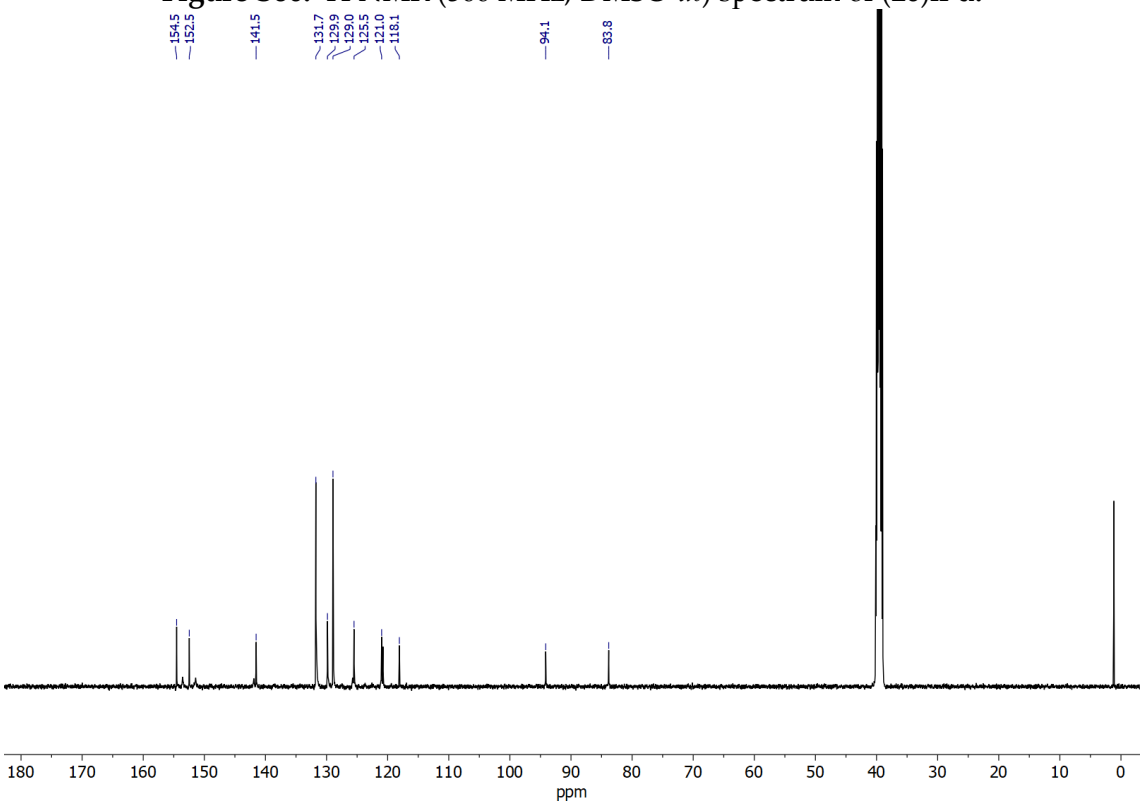


Figure S81. ^{13}C NMR (126 MHz, DMSO-d_6) spectrum of (**20**)$_2$Pd.

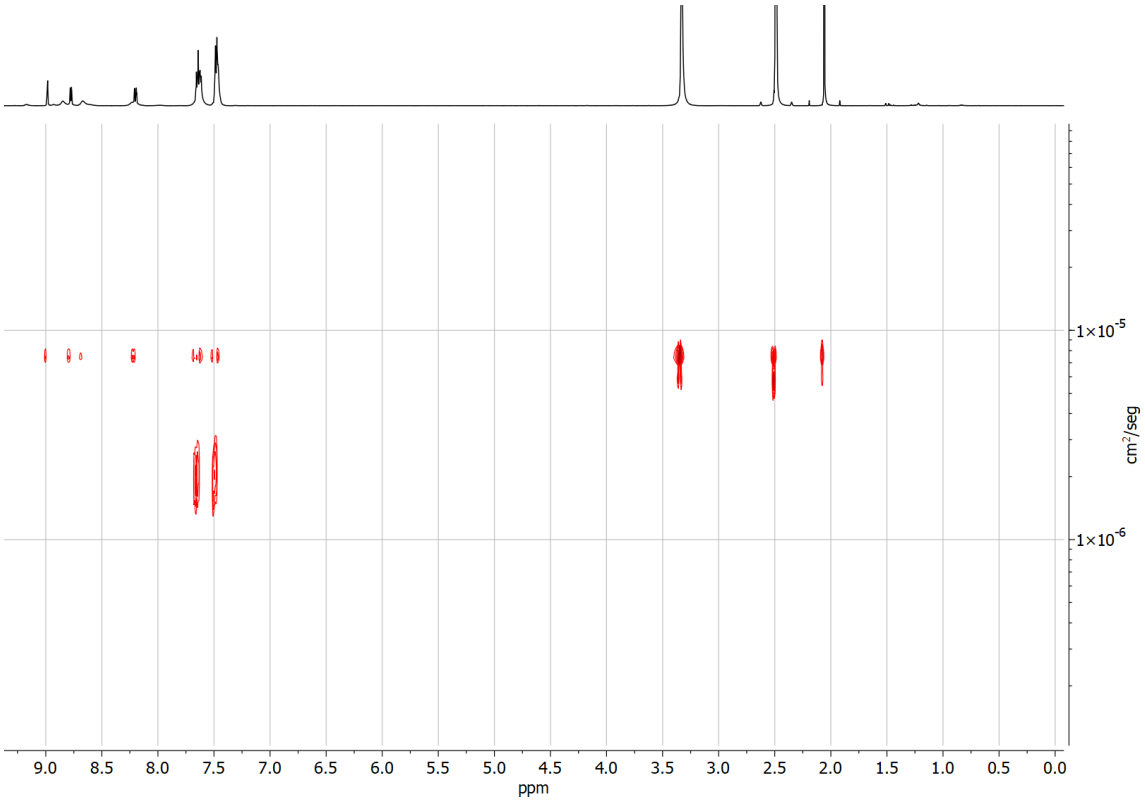


Figure S82. DOSY NMR (500 MHz, DMSO-d_6) spectrum of (**20**)$_2$Pd.

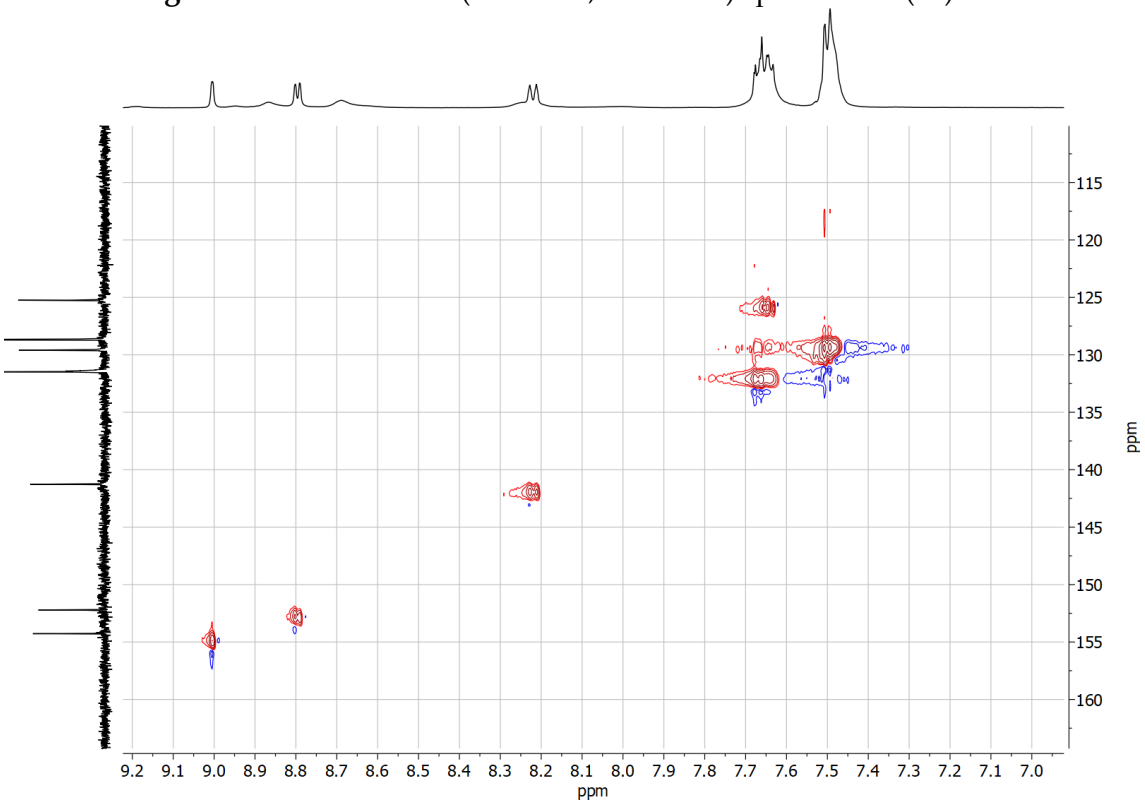


Figure S83. HSQC NMR (500 MHz and 126 MHz, DMSO-d_6) spectrum of (**20**)$_2$Pd.

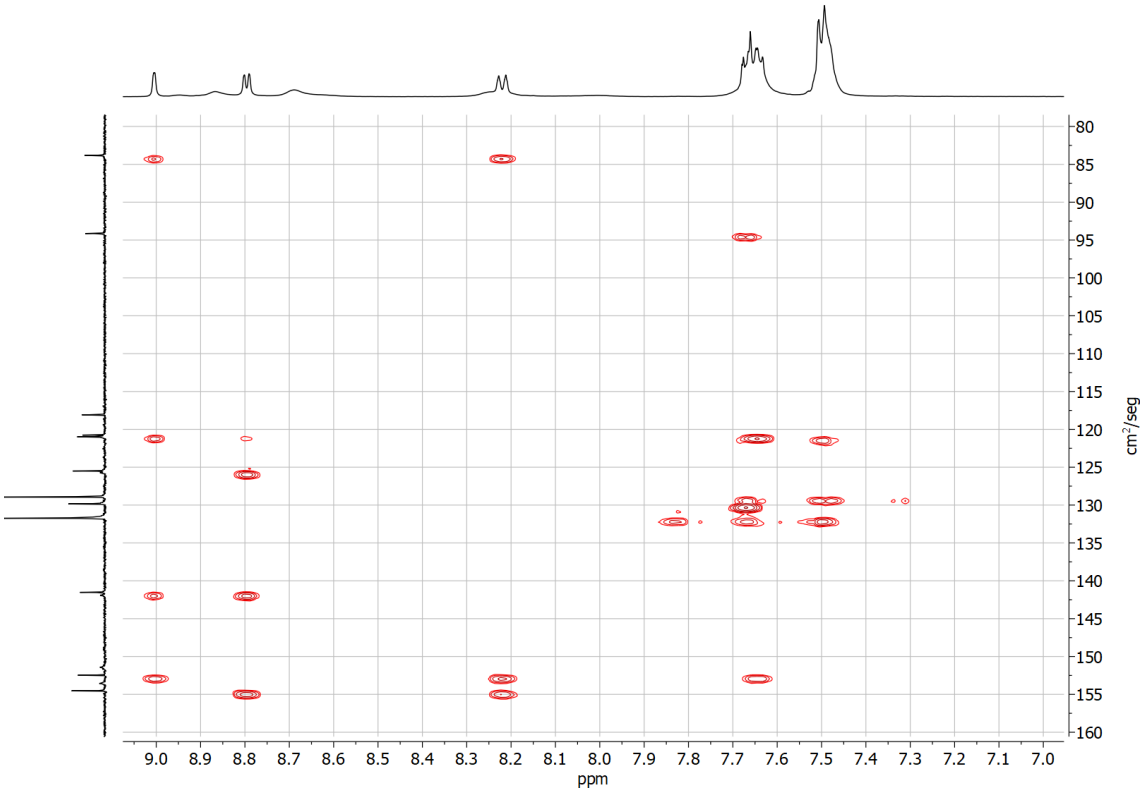


Figure S84. HMBC NMR (500 MHz and 126 MHz, DMSO-d_6) spectrum of (**20**)$_2$Pd.

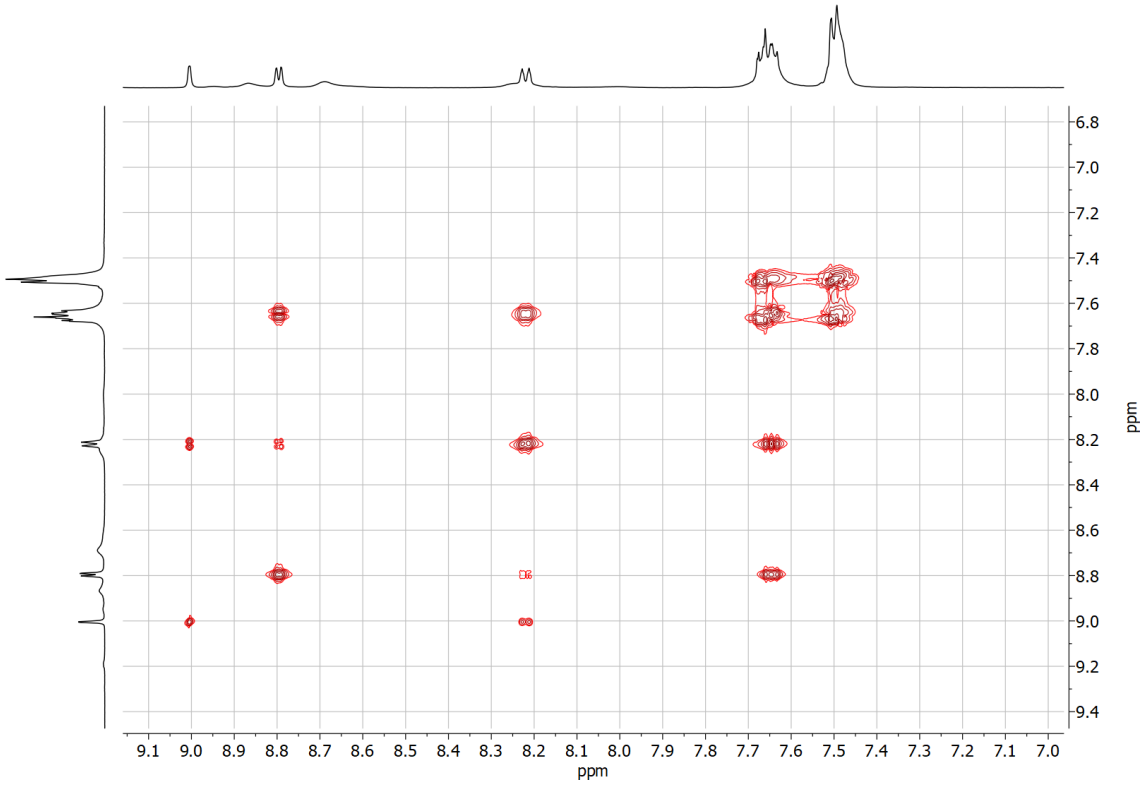


Figure S85. COSY NMR (500 MHz, DMSO-d_6) spectrum of (**20**)$_2$Pd.

3. STUDY OF THE METAL COORDINATION BY ^{1}H NMR

Study of the (S,S,P)-1-7:Ag(I) coordination by ^{1}H NMR

The corresponding compounds (*S*,*S*,*P*)-**N** (N=1-7) (0.024 mmol, 1 eq.) were dissolved in a 9:1 mixture of CD_2Cl_2: Acetone-d_6 (0.5 mL). On the other hand, a solution of $AgBF_4$ (0.120 mmol, 5 eq.) in 9:1 CD_2Cl_2: Acetone-d_6 (0.5 mL) was prepared. Stepwise additions of 1 eq. (0.1 mL) of metal was performed and the corresponding a ^{1}H-NMR spectra recorded. Changes in the aromatic signals confirmed the binding phenomena (see Figures 86-92). (*S*,*S*,*P*)-**7**:Ag(I) is only partially soluble in CD_2Cl_2, so it was necessary to make this titration adding only 1 eq (0.024 mmol, 0.5 mL) of metal (see Figure 92).

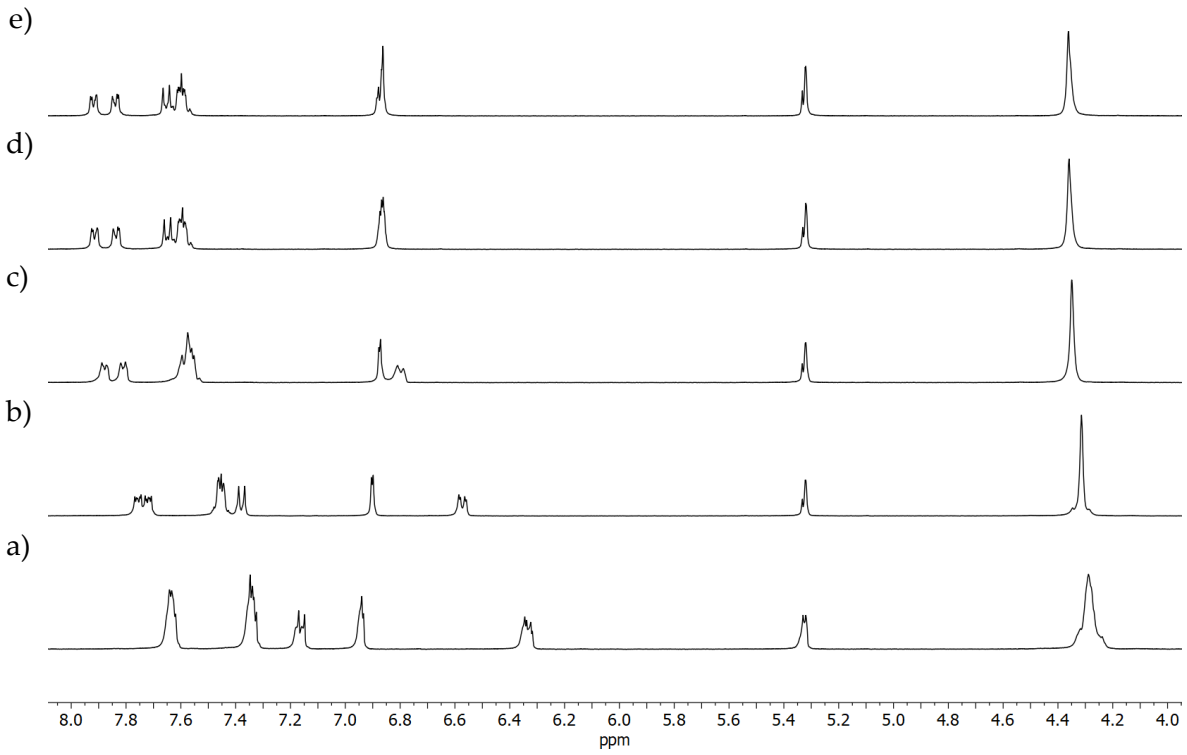


Figure S86. ^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectra for the titration of (*S*,*S*,*P*)-**1**:Ag(I), after addition of: a) 0 eq. b) 1 eq. c) 2 eq. d) 3 eq. e) 4 eq. of a solution of $AgBF_4$.

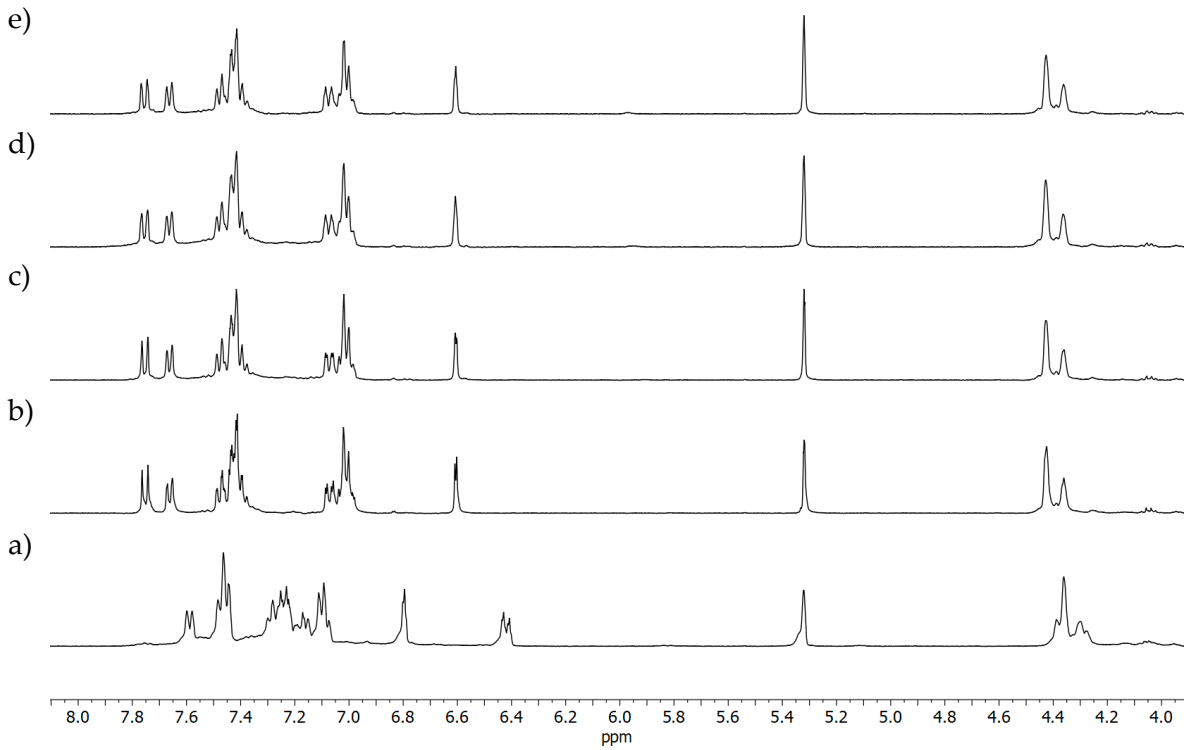


Figure S87. ^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectra for the titration of (*S*,*S*,*P*)-**2**:Ag(I), after addition of: a) 0 eq. b) 1 eq. c) 2 eq. d) 3 eq. e) 4 eq. of a solution of $AgBF_4$.

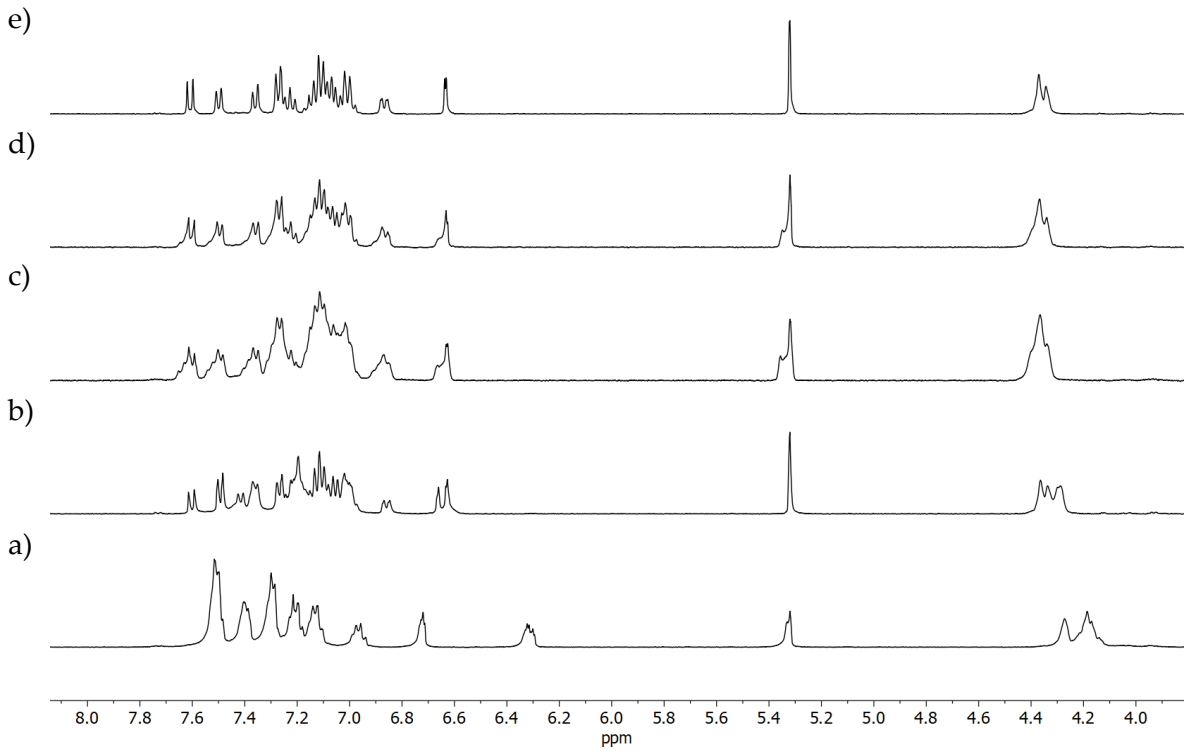


Figure S88. ^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectra for the titration of (*S*,*S*,*P*)-**3**:Ag(I), after addition of: a) 0 eq. b) 1 eq. c) 2 eq. d) 3 eq. e) 4 eq. of a solution of $AgBF_4$.

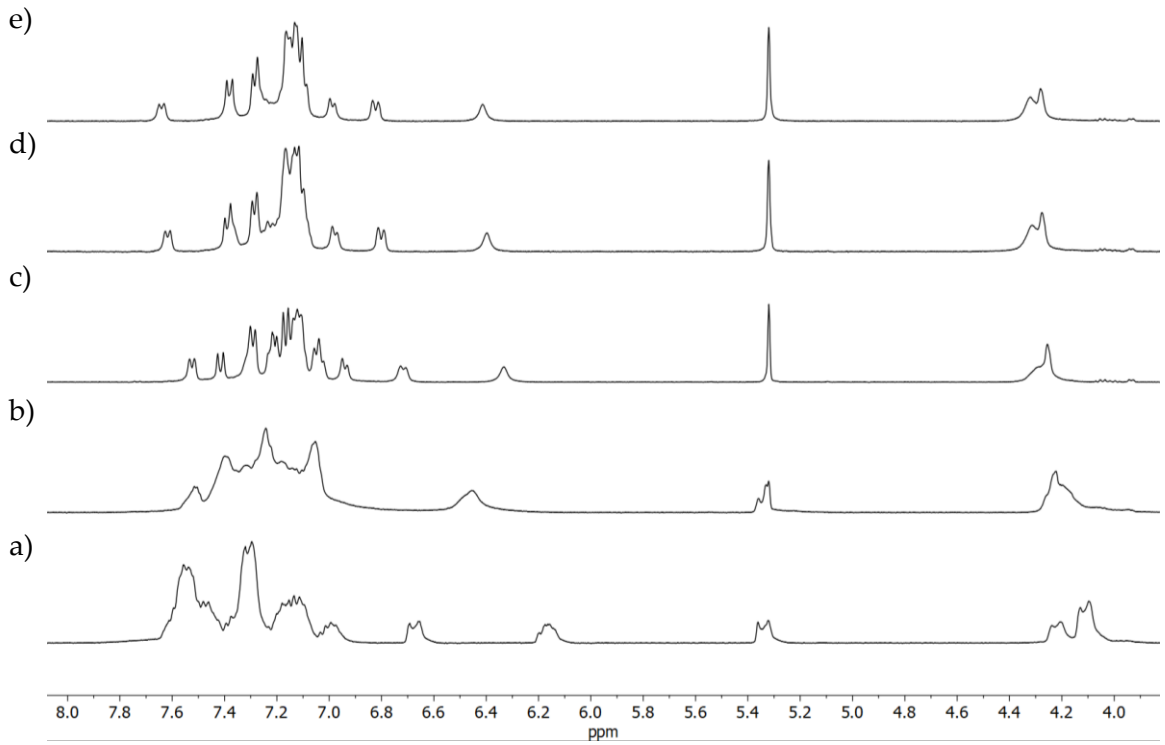


Figure S89. ^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectra for the titration of (*S*,*S*,*P*)-**4**:Ag(I), after addition of: a) 0 eq. b) 1 eq. c) 2 eq. d) 3 eq. e) 4 eq. of a solution of $AgBF_4$.

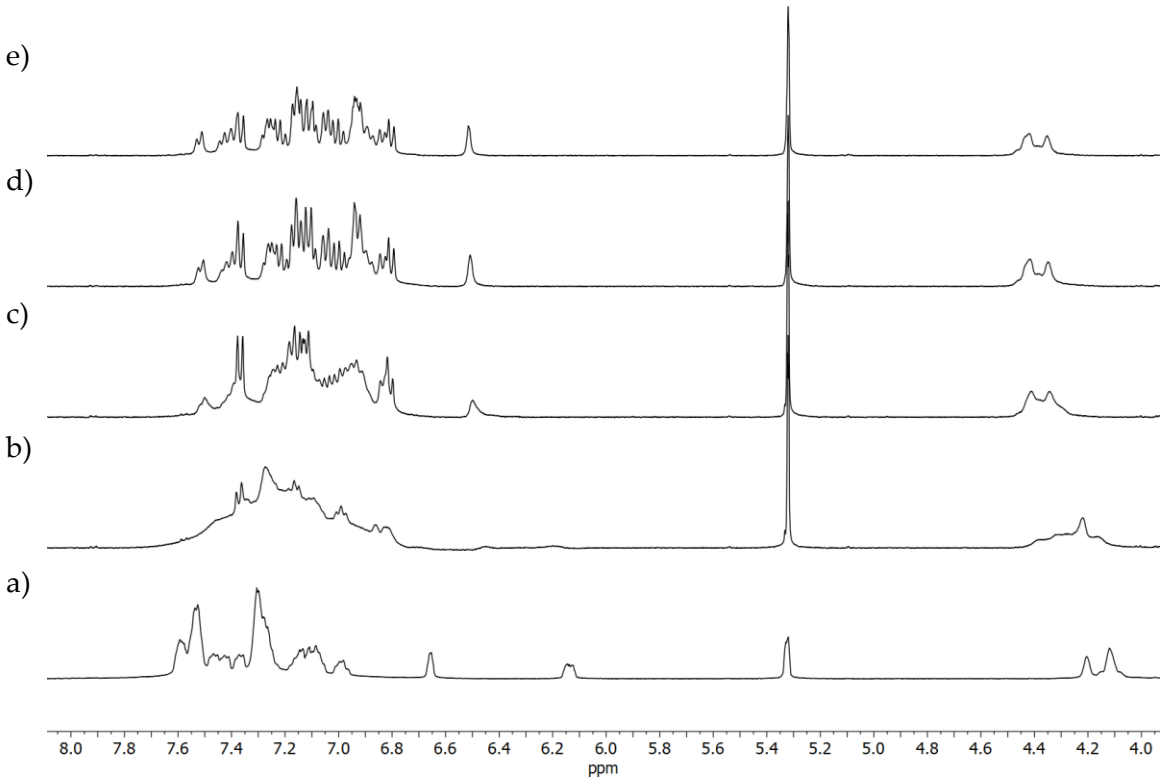


Figure S90. ^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectra for the titration of (*S*,*S*,*P*)-**5**:Ag(I), after addition of: a) 0 eq. b) 1 eq. c) 2 eq. d) 3 eq. e) 4 eq. of a solution of $AgBF_4$.

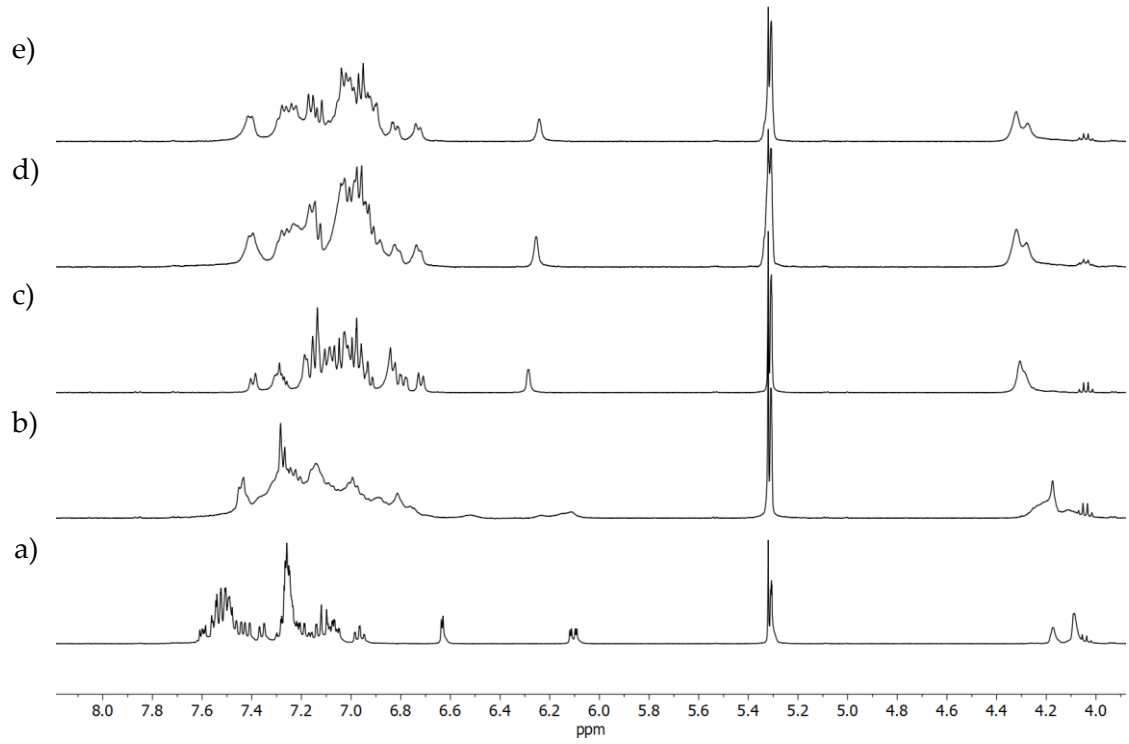


Figure S91. ^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectra for the titration of (*S*,*S*,*P*)-**6**:Ag(I), after addition of: a) 0 eq. b) 1 eq. c) 2 eq. d) 3 eq. e) 4 eq. of a solution of $AgBF_4$.

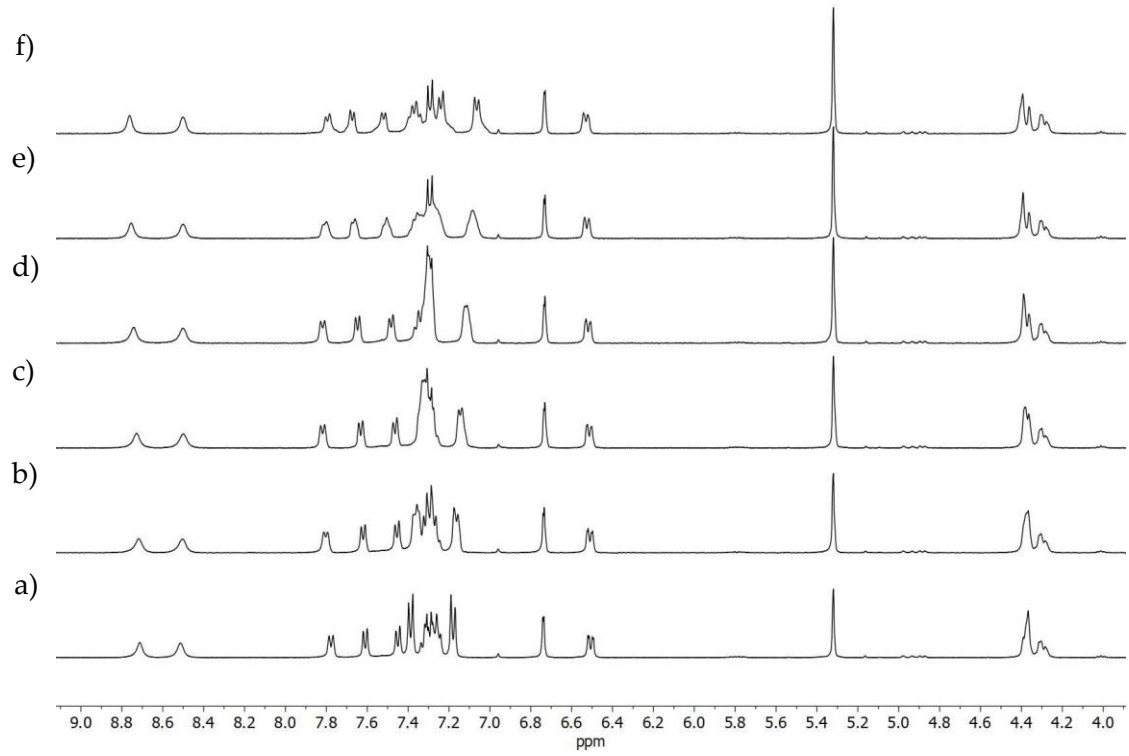


Figure S92. ^{1}H NMR (400 MHz, 9:1 CD_2Cl_2:Acetone-d_6) spectra for the titration of (*S*,*S*,*P*)-**7**:Ag(I), after addition of: a) 0 eq. b) 0.2 eq. c) 0.4 eq. d) 0.6 eq. e) 0.8 eq f) 1 eq. of a solution of $AgBF_4$.

Study of the (S,S,P)-7:Pd(II) and 20:Pd(II) coordination by ^{1}H NMR

A solution of (*S*,*S*,*P*)-**7** (10 mM) in CD_2Cl_2 was prepared. On the other hand, a solution of $Pd(CH_3CN)_2Cl_2$ (10 mM) in CD_2Cl_2 was prepared. Stepwise additions of metal was performed and the corresponding ^{1}H-NMR spectra recorded until complete ligand-metal coordination (see Figure S93). However, during this titration, a precipitate appeared. For this reason, we decided to study the coordination of (*S*,*S*,*P*)-**7**:Pd(II) in a different solvent where the final complex was totally soluble (DMSO-d_6) (see Figure S98). In this case, the method was the same than in CD_2Cl_2, and both solutions were prepared in the same concentration (10 mM). To confirm that the coordination is taking place in the pyridine, the same study of the Pd(II) coordination was performed with the model compound **20** (see Figures 105 and 106). In addition, to study the stability of this coordination, (*S*,*S*,*P*)-**7**:Pd(II) was monitored over time both CD_2Cl_2 and DMSO-d_6 in different concentrations (see Figures S94-97 and S99-S102).

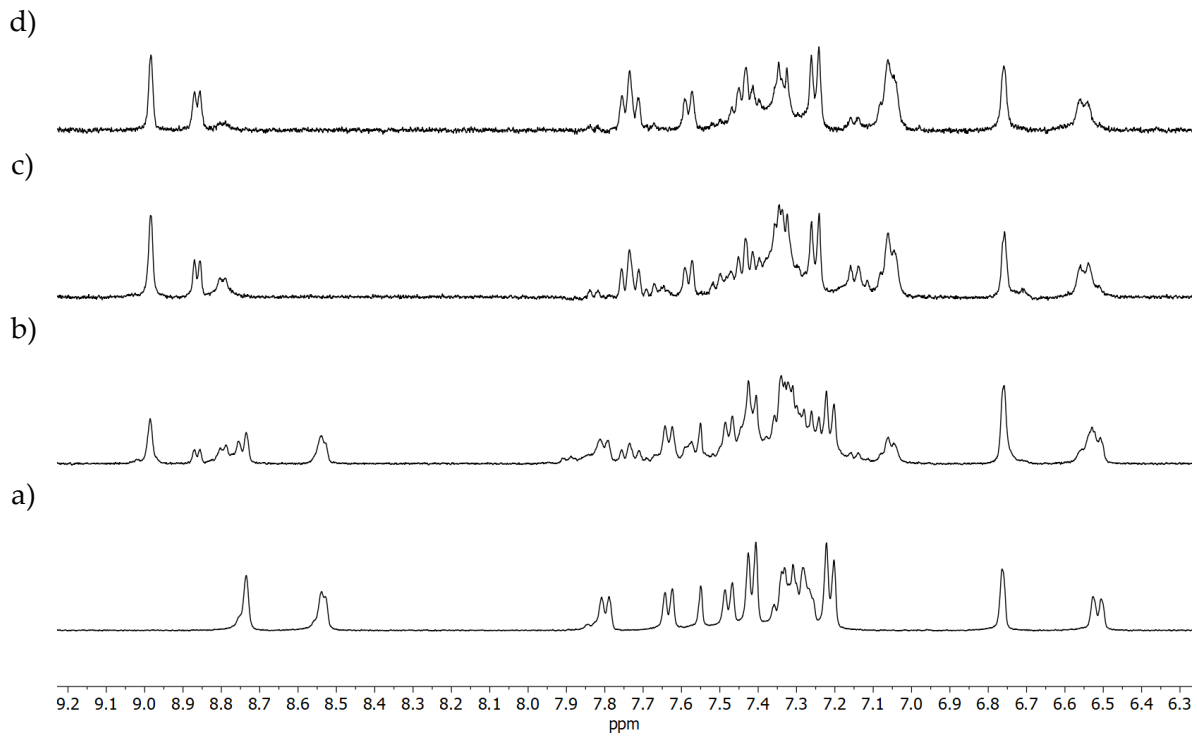


Figure S93. ^{1}H NMR (400 MHz, CD_2Cl_2) spectra for the titration of (*S*,*S*,*P*)-**7** (10 mM), after addition of: a) 0 mL, 0 eq. b) 0.2 mL, 0.4 eq. c) 0.4 mL, 0.8 eq. d) 0.6 mL, 1.2 eq. of a solution of $Pd(CH_3CN)_2Cl_2$ (10 mM).

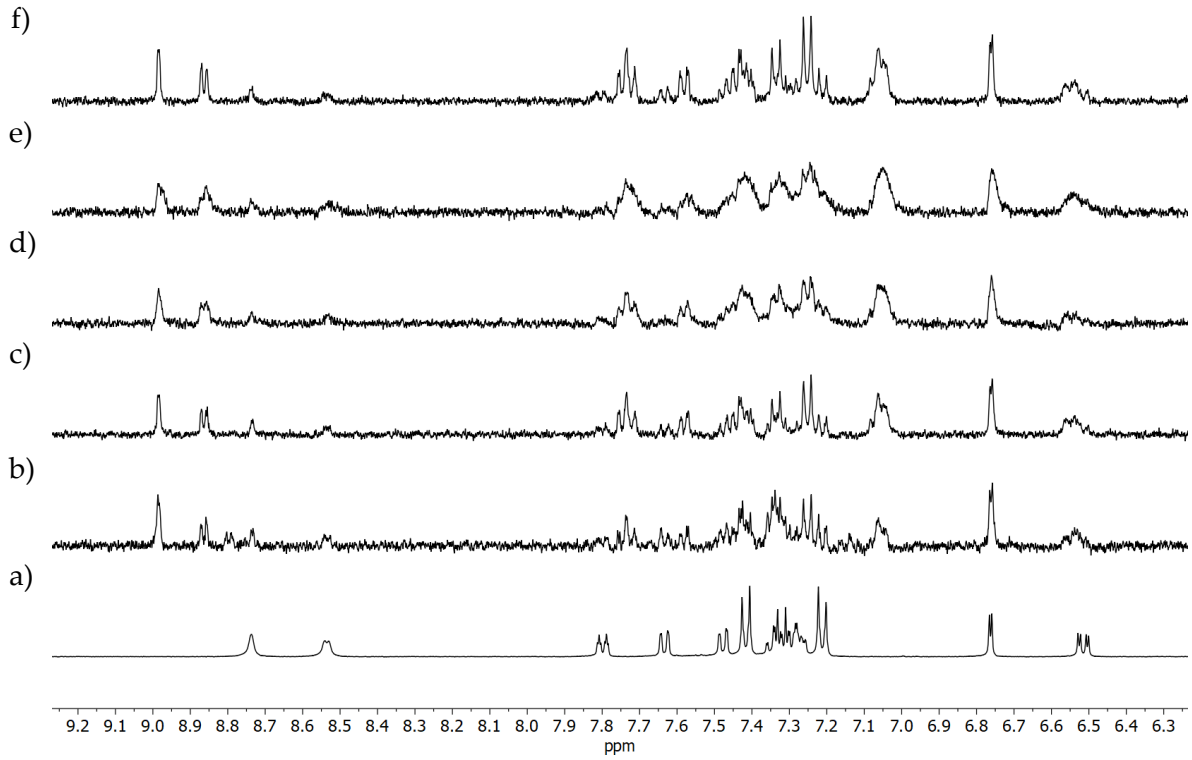


Figure S94. ^{1}H NMR (400 MHz, CD_2Cl_2) spectra of: a) (*S*,*S*,*P*)-**7** (5 mM). b) (*S*,*S*,*P*)-**7**:Pd(II) (0.5 mM); c) solution b after 24 h, d) solution b after 48 h, e) solution b after 72 h, f) solution b after 6 days.

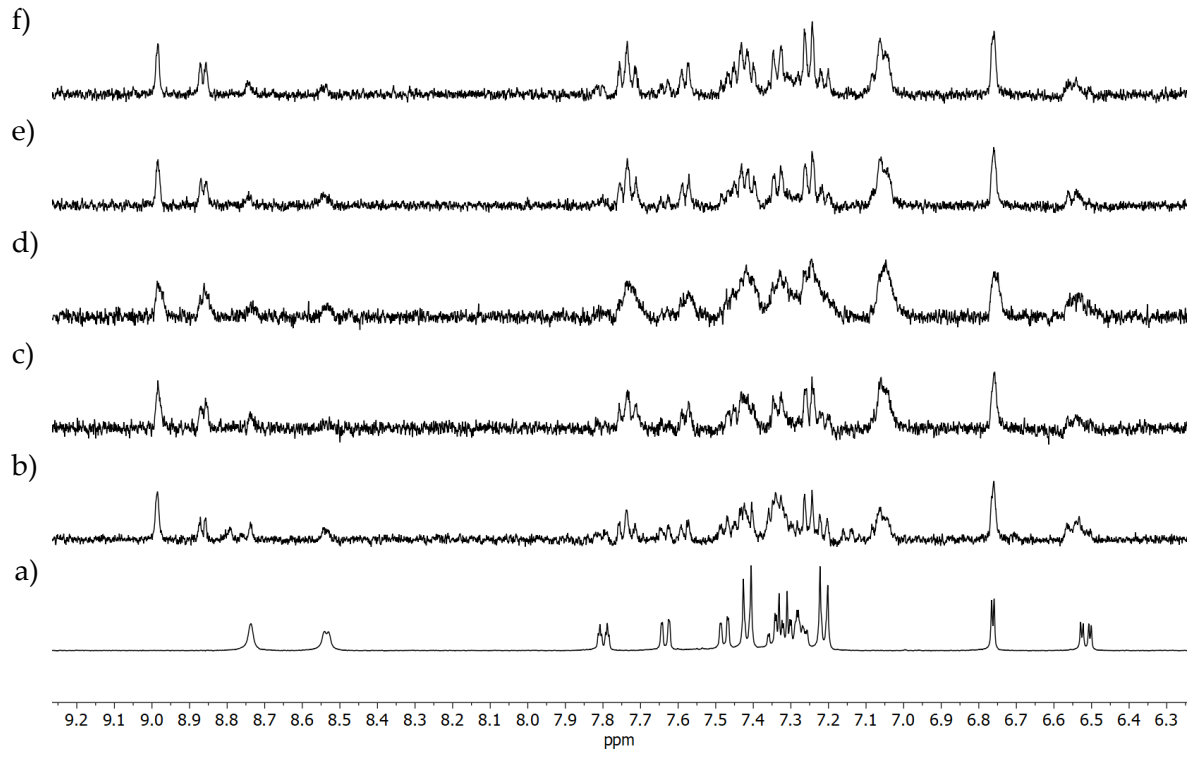


Figure S95. ^{1}H NMR (400 MHz, CD_2Cl_2) spectra of: a) (*S*,*S*,*P*)-**7** (5 mM). b) (*S*,*S*,*P*)-**7**:Pd(II) (1 mM); c) solution b after 24 h, d) solution b after 48 h, e) solution b after 72 h, f) solution b after 6 days.

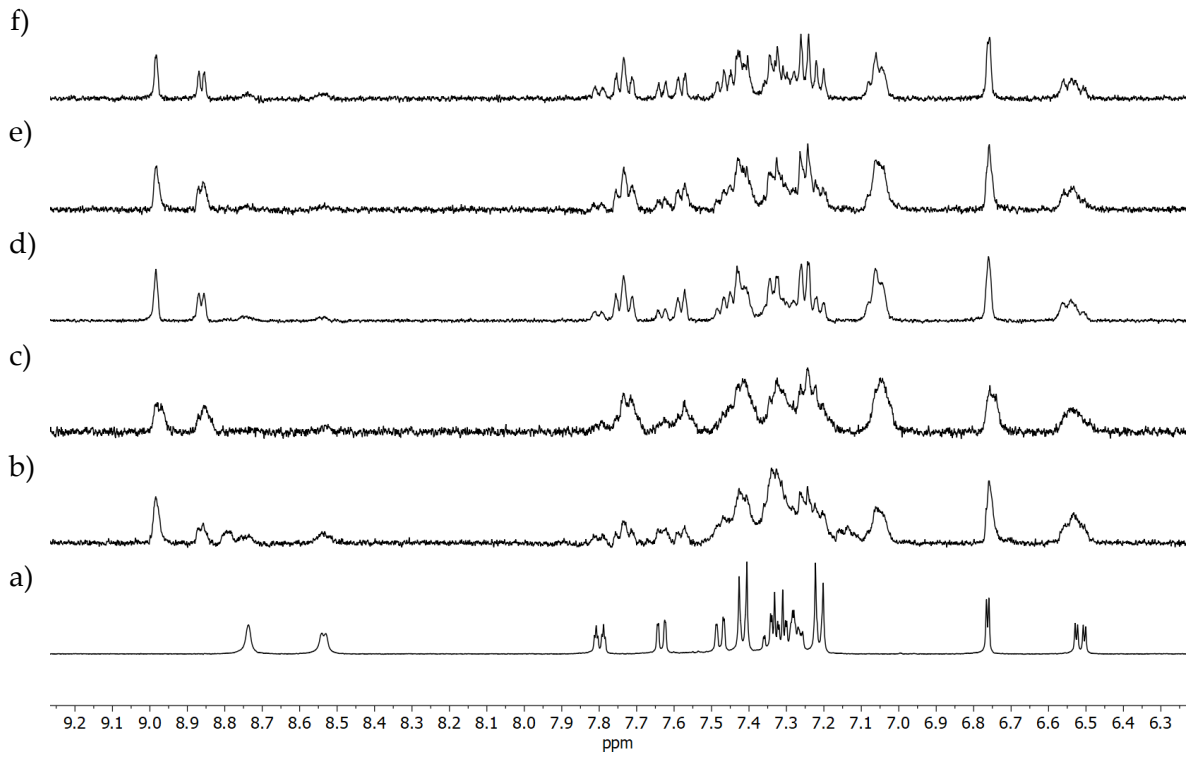


Figure S96. ^{1}H NMR (400 MHz, CD_2Cl_2) spectra of: a) (*S*,*S*,*P*)-**7** (5 mM). b) (*S*,*S*,*P*)-**7**:Pd(II) (2.5 mM); c) solution b after 24 h, d) solution b after 48 h, e) solution b after 72 h, f) solution b after 6 days.

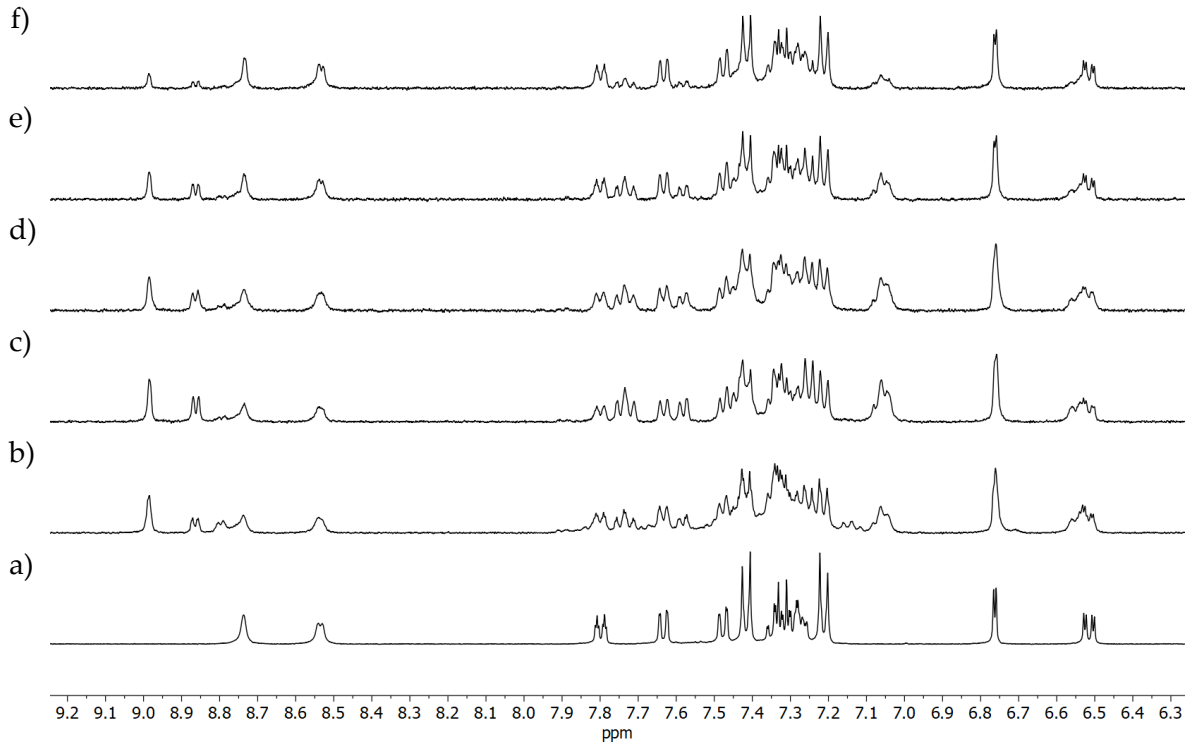


Figure S97. ^{1}H NMR (400 MHz, CD_2Cl_2) spectra of: a) (*S*,*S*,*P*)-**7** (5 mM). b) (*S*,*S*,*P*)-**7**:Pd(II) (5 mM); c) solution b after 24 h, d) solution b after 48 h, e) solution b after 72 h, f) solution b after 6 days.

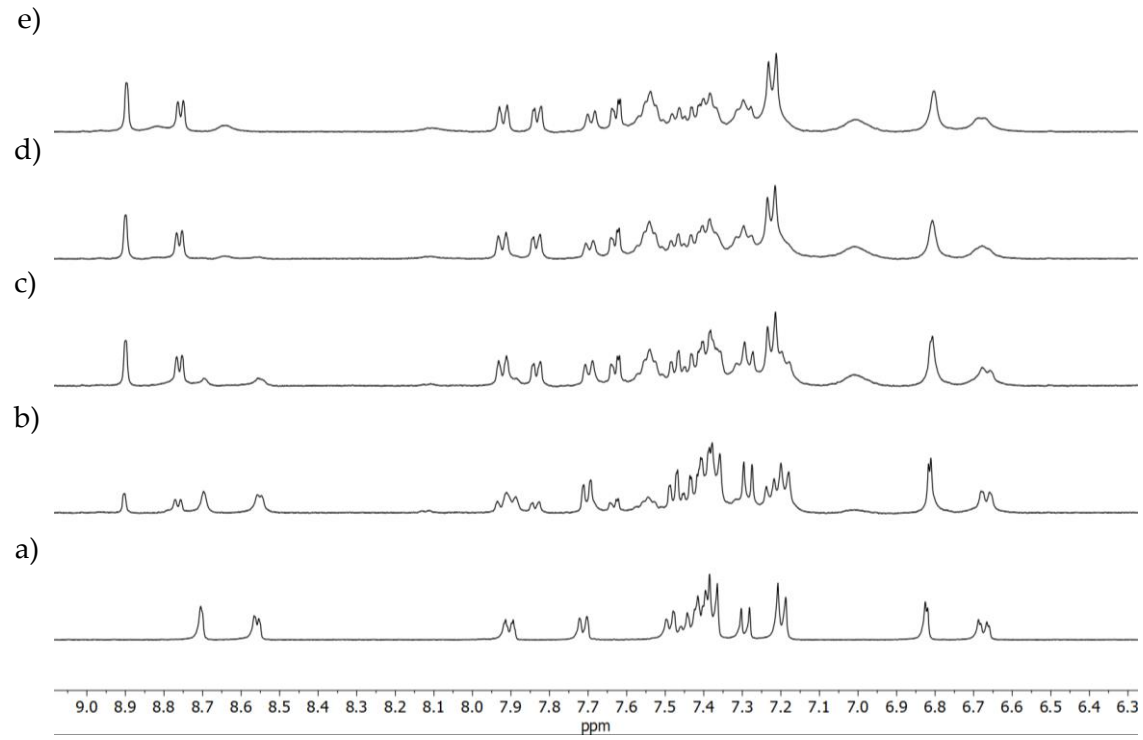


Figure S98. ^{1}H NMR (400 MHz, DMSO-d_6) spectra for the titration of (*S*,*S*,*P*)-**7** (10 mM), after addition of: a) 0 mL, 0 eq. b) 0.1 mL, 0.25 eq. c) 0.2 mL, 0.5 eq. d) 0.3 mL, 0.75 eq. e) 0.4 mL, 1 eq. of a solution of $Pd(CH_3CN)_2Cl_2$ (10 mM).

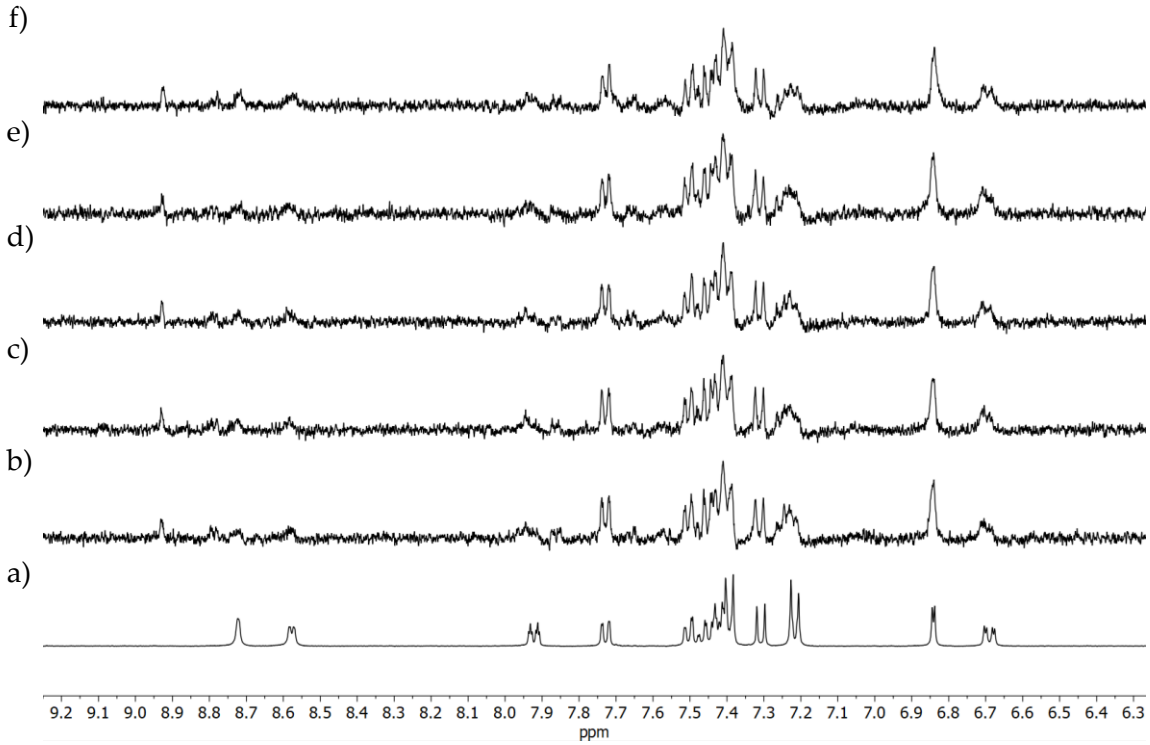


Figure S99. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of: a) (*S*,*S*,*P*)-**7** (5 mM). b) (*S*,*S*,*P*)-**7**:Pd(II) (0.5 mM); c) solution b after 24 h, d) solution b after 48 h, e) solution b after 72 h, f) solution b after 6 days.

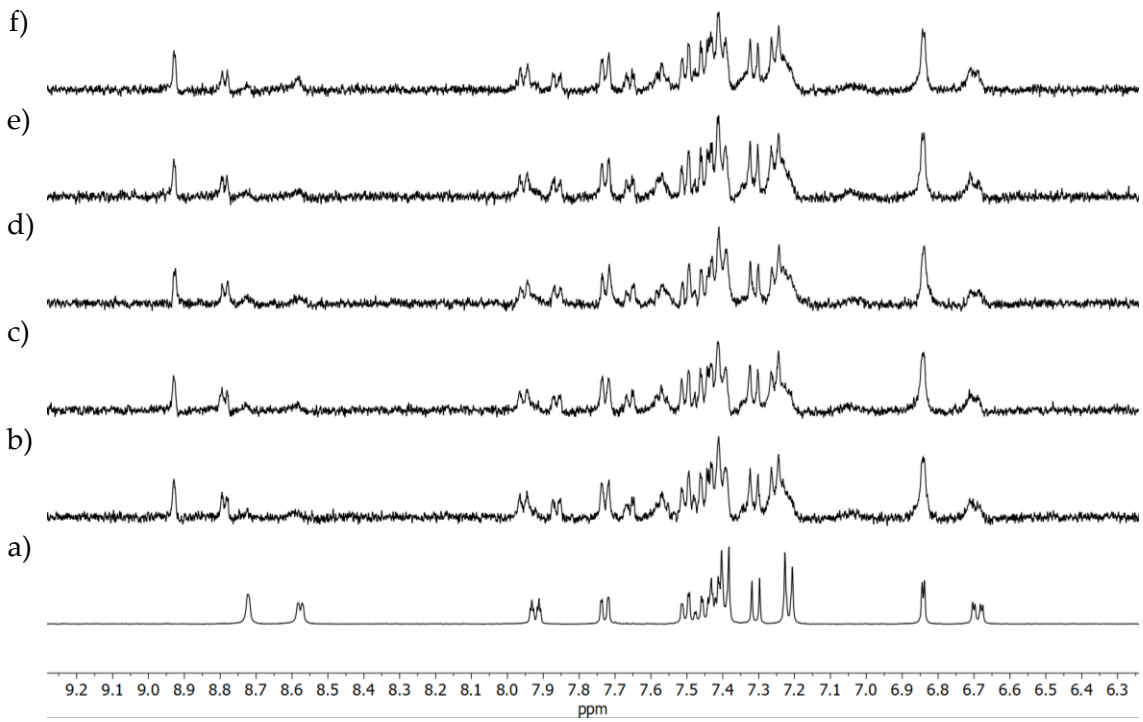


Figure S100. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of: a) (*S*,*S*,*P*)-**7** (5 mM). b) (*S*,*S*,*P*)-**7**:Pd(II) (1 mM); c) solution b after 24 h, d) solution b after 48 h, e) solution b after 72 h, f) solution b after 6 days.

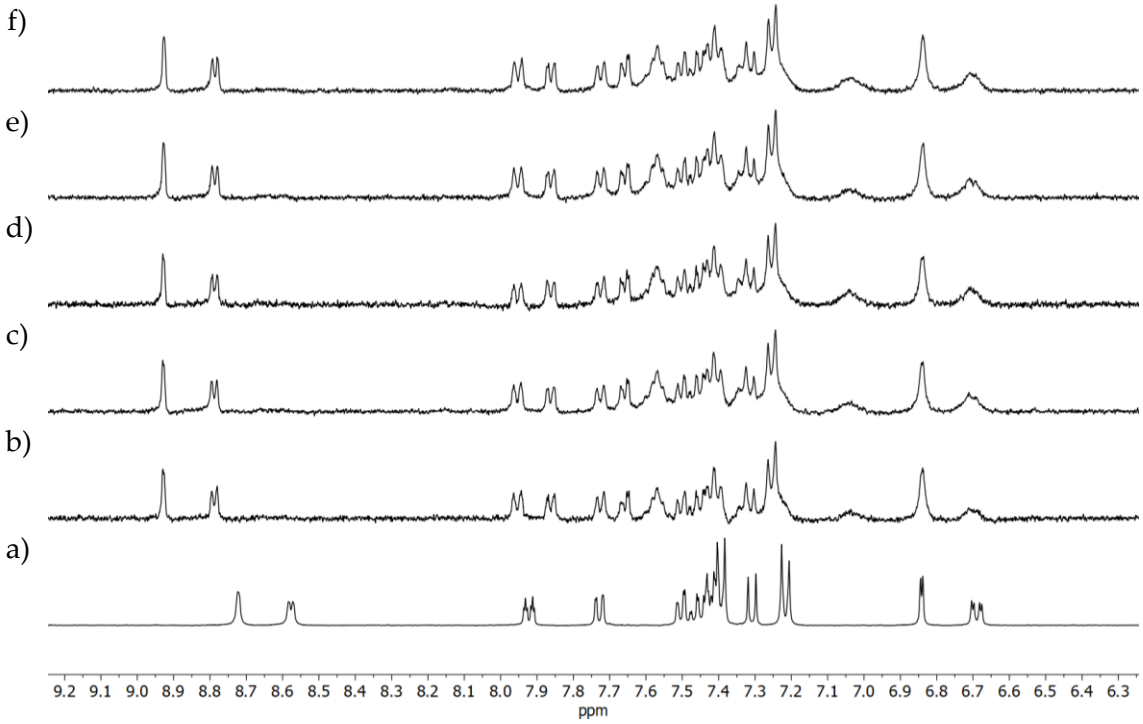


Figure S101. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of: a) (*S*,*S*,*P*)-**7** (5 mM). b) (*S*,*S*,*P*)-**7**:Pd(II) (2.5 mM); c) solution b after 24 h, d) solution b after 48 h, e) solution b after 72 h, f) solution b after 6 days.

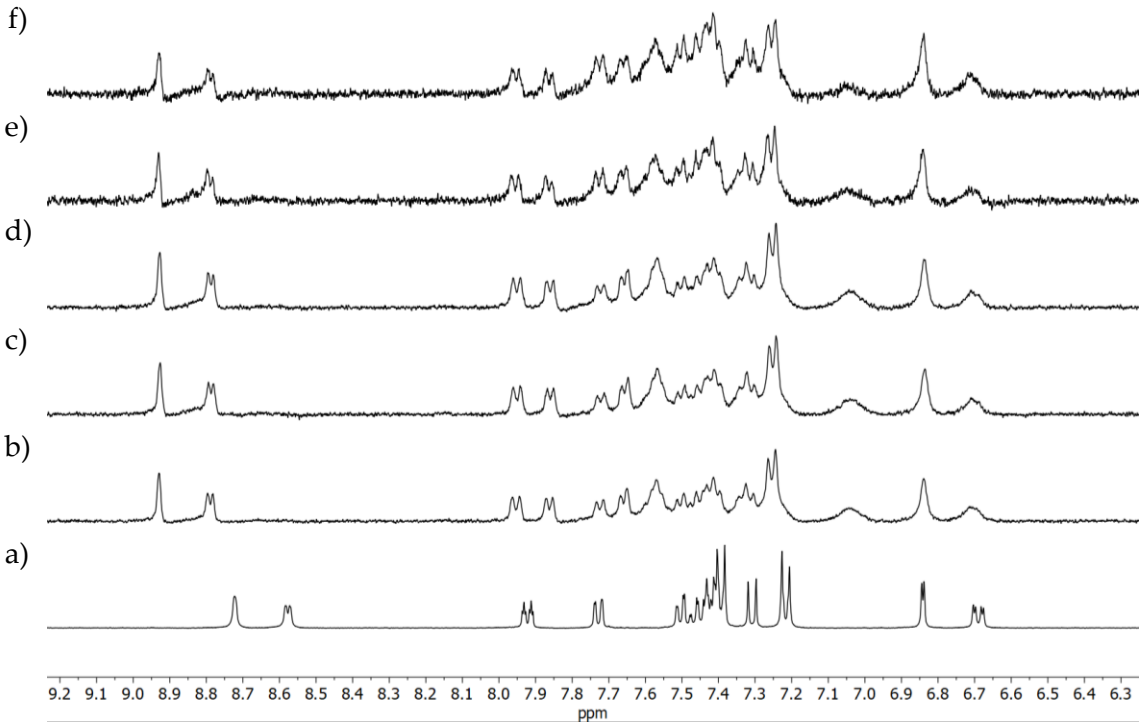


Figure S102. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of: a) (*S*,*S*,*P*)-**7** (5 mM). b) (*S*,*S*,*P*)-**7**:Pd(II) (5 mM); c) solution b after 24 h, d) solution b after 48 h, e) solution b after 72 h, f) solution b after 6 days.

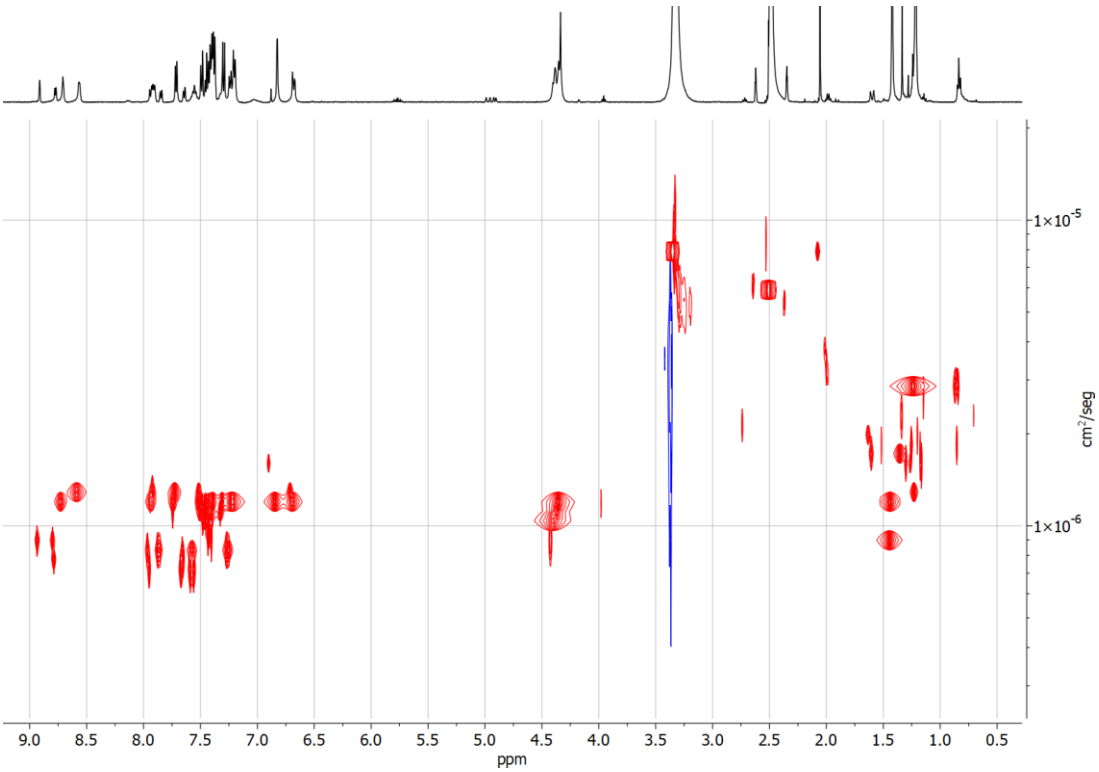


Figure S103. DOSY NMR (500 MHz, DMSO-d_6) spectrum of (*S*,*S*,*P*)-**7** (5 mM) after addition of 0.25 mL (0.5 eq) of a solution of $Pd(CH_3CN)_2Cl_2$ (5 mM).

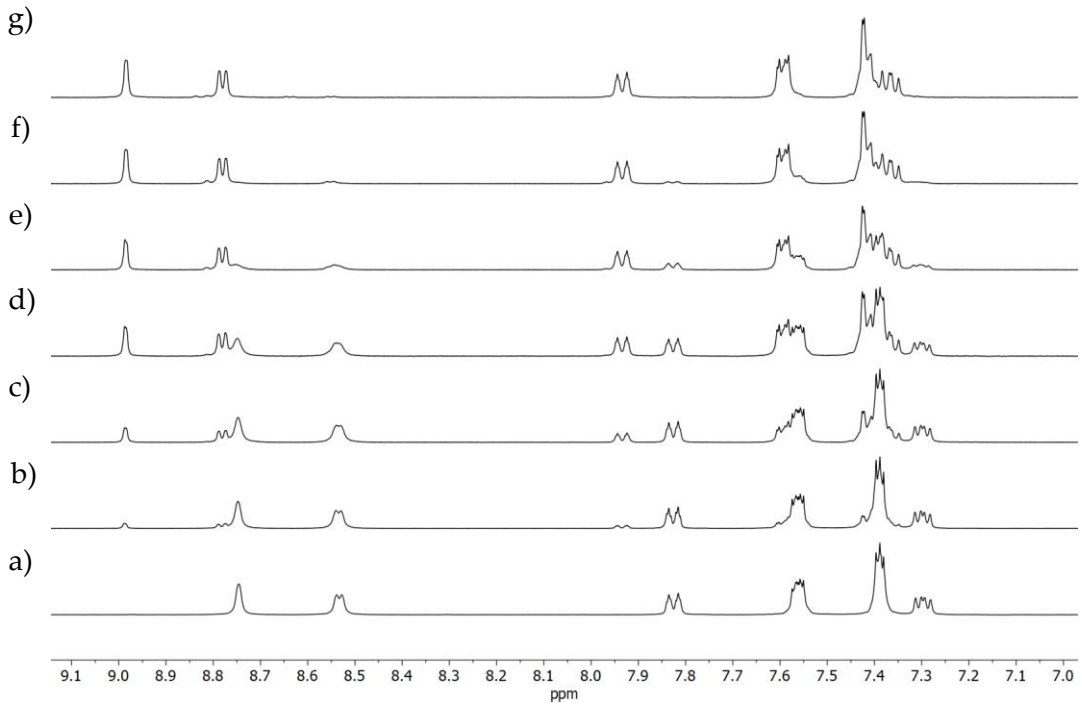


Figure S104. ^{1}H NMR (400 MHz, CD_2Cl_2) spectra for the titration of **20** (50 mM), after addition of: a) 0 mL, 0 eq. b) 0.1 mL, 0.16 eq. c) 0.2 mL, 0.33 eq. d) 0.3 mL, 0.5 eq. e) 0.4 mL, 0.66 eq. f) 0.5 mL, 0.83 eq. g) 0.6 mL, 1 eq. of a solution of $Pd(CH_3CN)_2Cl_2$ (50 mM).

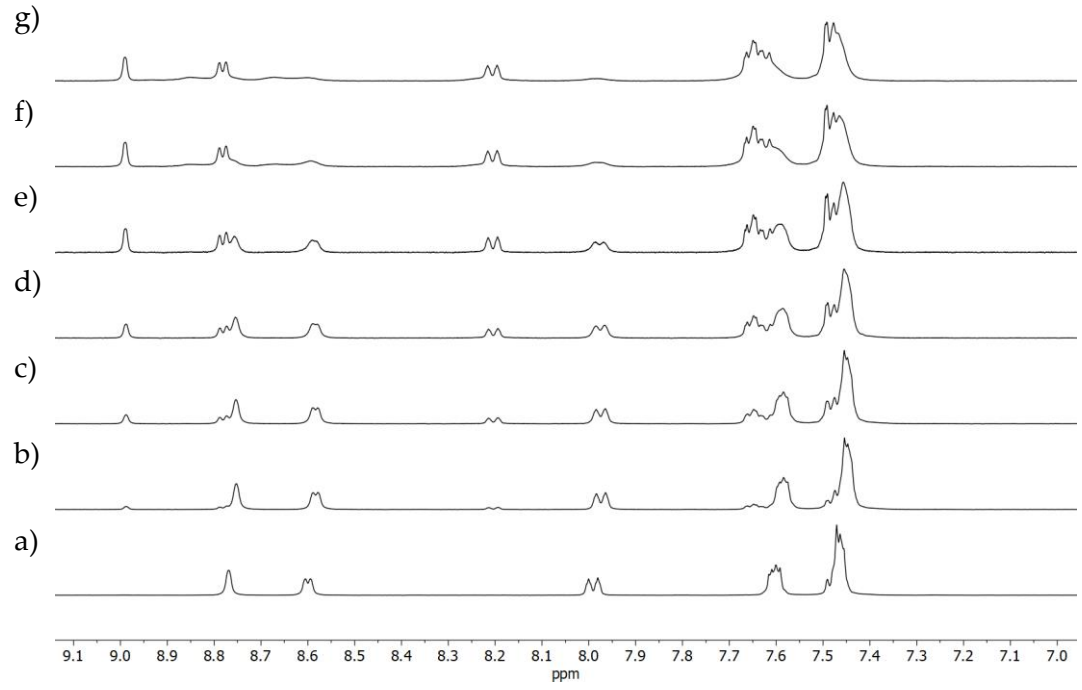


Figure S105. ^{1}H NMR (400 MHz, DMSO-d_6) spectra for the titration of **20** (50 mM), after addition of: a) 0 mL, 0 eq. b) 0.1 mL, 0.16 eq. c) 0.2 mL, 0.33 eq. d) 0.3 mL, 0.5 eq. e) 0.4 mL, 0.66 eq. f) 0.5 mL, 0.83 eq. g) 0.6 mL, 1 eq. of a solution of $Pd(CH_3CN)_2Cl_2$ (50 mM).

4. LIFETIMES, QUANTUM YIELDS AND TRES DECONVOLUTION OF COMPOUNDS (*S,S,P*)-1-7

Quantum yields were determined by measuring both absorbance and fluorescence of compounds (*S,S,P*)-**1**-**7** quinine sulphate in 0.1 M H_2SO_4 as standard (Φr = 0.54).[9] For the relative determination of the fluorescence quantum yield Φ the following formula was used:[10]

$$\Phi_x = \Phi_r \, \mathrm{x} \, \frac{F_x}{F_r} \, \mathrm{x} \, \frac{1-10^{-A_r(\lambda_{ex})}}{1-10^{-A_x(\lambda_{ex})}} \, \mathrm{x} \, \frac{n_x^2}{n_r^2} \qquad \text{(eq. S1)}$$

The subscripts ***x*** and ***r*** refer respectively to sample and reference (standard) fluorophore with known quantum yield Φ_r in a specific solvent; *F* stands for the spectrally corrected, integrated fluorescence spectra; $A(\lambda_{ex})$ denotes the absorbance at the used excitation wavelength λ_{ex}; and *n* represents the refractive index of the solvent (in principle at the average emission wavelength). To minimize inner filter effects, the absorbance at the excitation wavelength λ_{ex} was kept under 0.1. The measurements were performed using 10×10 mm cuvettes on non-degassed samples.

Time-resolved fluorescence decay traces were collected via the time-correlated single photon counting (TCSPC) method using a FluoTime 200 fluoromoter (PicoQuant, GmbH). The excitation source was a 325-nm LED using a 20 MHz excitation frequency. The full width at half maximum (fwhm) of the laser pulses was around 40 ps. The fluorescence emission was collected at a 90° geometry, focused at the detector after crossing through a polarizer (set at the magic angle), 2-mm slits, and a 2-nm bandwidth monochromator. TCSPC was achieved by a TimeHarp200 board, set at 36 ps/channel. Fluorescence decay traces were collected for the necessary time to reach 20,000 counts at the peak channel. For all the compounds decay traces were collected at 400,405 and 410nm, where the maximum of emission was observed.

Time-resolved emission spectroscopy (TRES) of compounds (*S,S,P*)-**2** and (*S,S,P*)-**5** was performed in four solvents (CH_2Cl_2, CH_3CN, MeOH and hexane) by collecting 65 fluorescence decay traces in the 340-600 nm emission range ($\Delta\lambda_{em}$ = 5 nm) at 20 MHz excitation frequency during a fixed amount of time (500 s), to maintain the overall intensity information.

The fluorescence decay traces were fitted to a bi-, three- or four-exponential function, by using a Levenberg-Marquard algorithm-based nonlinear least-squares error minimization deconvolution method iterative reconvolution methods (FluoFit 4.4 package, Picoquant GmbH). For each sample, the decay traces were fitted globally with the decay times linked as shared parameters, whereas the pre-exponential factors were local adjustable parameters. The quality of fittings was assessed by the value of the reduced chi-squared, χ^2, parameter and random distributions of the weighted residuals and the autocorrelation functions.

For the TRES (Time Resolved Emission Spectroscopy) analysis and the estimation of the species-associated emission spectra (SAEMS), the fitting procedure described above was performed, by fitting globally the 61 decay traces. The SAEMS of each species *i* at any given emission wavelength ($SAEMS_i(\lambda_{em})$) is given by the fluorescence intensity emitted by the species *i* ($A_{i,\lambda em} \times \tau_i$), normalized by the total intensity and corrected for the different detection sensitivity using the total intensity of the steady-state spectrum ($I_{ss,\lambda em}$):

$$SAEMS_i(\lambda_{em}) = \frac{A_{i,\lambda em} \times \tau_i}{\sum_i A_{i,\lambda em} \times \tau_i} \cdot I_{ss,\lambda em} \qquad \text{(eq. S2)}$$

The approximate contribution of each species can be assessed as the area under the SAEMS. This estimation assumes equal excitation rate for all the species, as the initial amount of each form in the excited state (after the pulse excitation) is unknown. Figures S107-S108 show the SAEMS of compounds (*S,S,P*)-**2** and (*S,S,P*)-**5** in different solvents.

Table S1. Fluorescence lifetimes (average of signals at 400, 405 and 410 nm) of compounds (*S,S,P*)-**1-7** in CH_2Cl_2 solutions.

COMPOUND	τ_1	τ_2	$\tau_{average}$
(*S,S,P*)-**1**	0.711±0.004	0.1786±0.0082	0.642
(*S,S,P*)-**2**	4.288±0.010	2.319±0.036	4.0382
(*S,S,P*)-**3**	4.542±0.021	2.62±0.02	3.7822
(*S,S,P*)-**4**	4.63±0.019	2.587±0.024	3.96
(*S,S,P*)-**5**	4.198±0.017	1.647±0.032	3.52
(*S,S,P*)-**6**	4.398±0.017	1.691±0.027	3.796
(*S,S,P*)-**7**	4.394±0.020	2.492±0.0021	3.67

Table S2. Quantum yields and fluorescence lifetimes (average of signals at 400, 405 and 410 nm) of compound (*S,S,P*)-**1** in different solvents.

SOLVENT	Φ	τ_1	τ_2	$\tau_{average}$
CH_2Cl_2	4.56±0.09	0.711±0.004	0.1786±0.0082	0.6422
Acetone	-	1.952±0.021	0.673±0.0069	1.1307
AcOEt	4.72±0.06	2.71±0.28	0.6682±0.0036	0.696
CH_3CN	3.27±0.07	0.8377±0.0006	0.512±0.012	0.7474

Et_2O	6.10±0.09	3.695±0.034	0.6537±0.0055	1.6902
Hexane	5.63±0.11	1.136±0.085	0.5517±0.0033	0.5733
MeOH	2.94±0.44	1.06±0.037	0.65±0.0041	0.6921
THF	4.70±0.44	3.91±0.25	0.6767±0.004	0.747
Toluene	6.24±0.51	4.086±0.39	0.6355±0.0032	0.674

Table S3. Quantum yields and fluorescence lifetimes (average of signals at 400, 405 and 410 nm) of compound (*S,S,P*)-**2** in different solvents.

SOLVENT	Φ	τ_1	τ_2	$\tau_{average}$
CH_2Cl_2	19.0±3.3	4.288±0.010	2.319±0.036	4.0382
Acetone	-	3.955±0.015	1.552±0.047	3.6848
AcOEt	22.9±1.1	3.805±0.014	2.105±0.037	3.499
CH_3CN	21.8±0.6	4.114±0.019	2.375±0.022	3.5163
Et_2O	34.0±1.1	4.20±0.015	2.259±0.037	3.8313
Hexane	23.9±0.5	3.554±0.015	2.202±0.023	3.1274
MeOH	23.9±0.2	4.236±0.018	2.452±0.022	3.6321
THF	29.1±4.6	3.964±0.015	2.131±0.034	3.5999
Toluene	26.1±0.6	3.6128±0.017	2.26±0.022	3.1231

Table S4. Quantum yields of compounds (*S,S,P*)-**3-7** in CH_2Cl_2, hexane, CH_3CN and methanol.

COMPOUND	CH_2Cl_2	Hexane	CH_3CN	MeOH
(*S,S,P*)-**3**	10.2±0.9	13.3±0.5	5.6±1.3	4.7±1.5
(*S,S,P*)-**4**	13.6±2.1	5.5±0.2	5.2±1	5.7±0.4
(*S,S,P*)-**5**	10.8±0.9	12.1±0.3	7.5±0.4	15.5±0.7
(*S,S,P*)-**6**	7.9±1.5	4.0±0.1	3.7±0.2	4.6±0.3
(*S,S,P*)-**7**	25.2±0.2	34.5±4.0	37.1±4.9	45.7±4.3

Table S5. Fluorescence lifetimes (average of signals at 400, 405 and 410 nm) (ns) of compounds (*S*,*S*,*P*)-**3-7** in CH_2Cl_2, hexane, CH_3CN and methanol.

COMPOUND	CH_2Cl_2	Hexane	CH_3CN	MeOH
(*S*,*S*,*P*)-**3**	τ_1 =4.542±0.021 τ_2 = 2.62±0.02 τ_{av} = 3.7822	τ_1 =3.951±0.02 τ_2 = 2.443±0.019 τ_{av} = 3.312	τ_1 =4.475±0.014 τ_2 = 2.082±0.055 τ_{av} = 4.2138	τ_1 =3.912±0.018 τ_2 = 1.584±0.024 τ_{av} = 3.2605
(*S*,*S*,*P*)-**4**	τ_1 =4.630±0.019 τ_2 = 2.587±0.024 τ_{av} = 3.96	τ_1 =3.824±0.016 τ_2 = 1.972±0.024 τ_{av} = 3.277	τ_1 =4.622±0.018 τ_2 = 1.88±0.046 τ_{av} = 4.218	τ_1 =4.772±0.016 τ_2 = 2.156±0.040 τ_{av} = 4.332
(*S*,*S*,*P*)-**5**	τ_1 =4.198±0.017 τ_2 = 1.647±0.032 τ_{av} = 3.517	τ_1 =3.805±0.014 τ_2 = 2.057±0.032 τ_{av} = 3.421	τ_1 =4.707±0.016 τ_2 = 1.701±0.014 τ_{av} = 4.3196	τ_1 =4.820±0.016 τ_2 = 2.333±0.048 τ_{av} = 4.470
(*S*,*S*,*P*)-**6**	τ_1=4.398±0.017 τ_2 = 1.691±0.027 τ_{av} = 3.796	τ_1 =3.715±0.015 τ_2 = 1.380±0.026 τ_{av} = 3.265	τ_1 =4.606±0.019 τ_2 = 1.261±0.026 τ_{av} = 4.01	τ_1 =4.730±0.017 τ_2 = 1.529±0.036 τ_{av} = 4.284
(*S*,*S*,*P*)-**7**	τ_1 =4.394±0.020 τ_2 = 2.492±0.021 τ_{av} = 3.664	τ_1 =3.636±0.016 τ_2 = 2.148±0.021 τ_{av} = 3.097	τ_1 =4.327±0.016 τ_2 = 2.449±0.031 τ_{av} = 3.850	τ_1 =4.443±0.019 τ_2 = 2.423±0.023 τ_{av} = 3.741

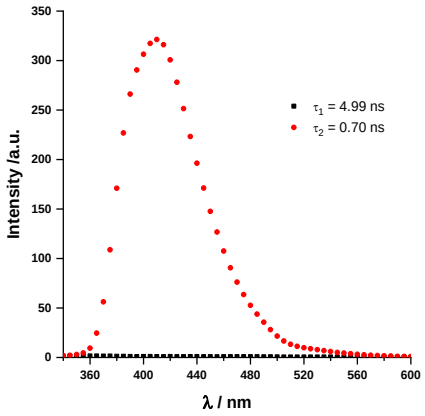


Figure S106. SAEMS spectra of compound (*S*,*S*,*P*)-**1** in CH_2Cl_2

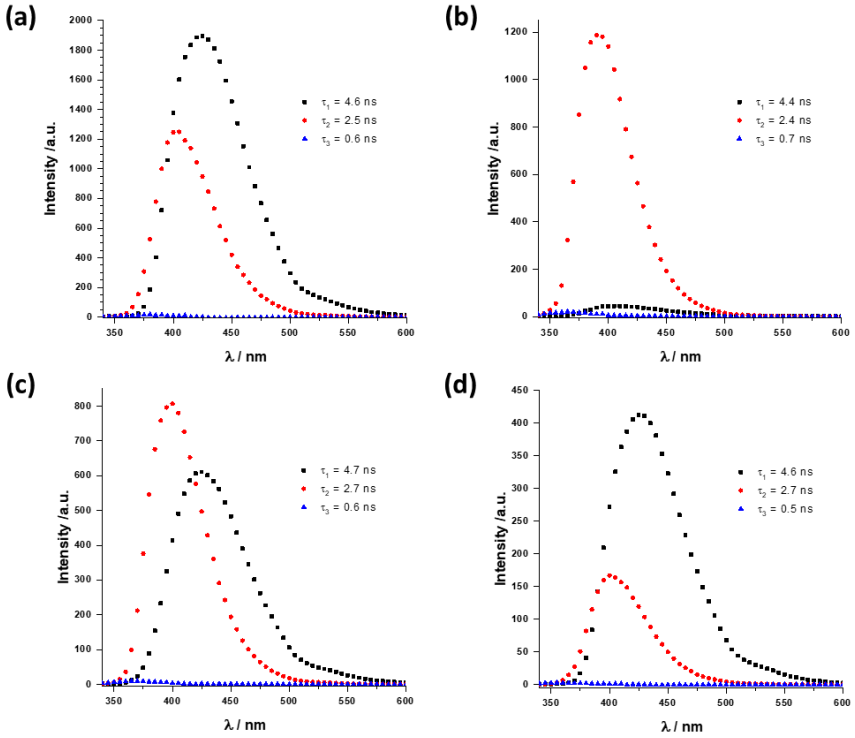


Figure S107. SAEMS spectra of compound (*S,S,P*)-**2** in (a) CH_2Cl_2, (b) hexane, (c) CH_3CN and (d) MeOH.

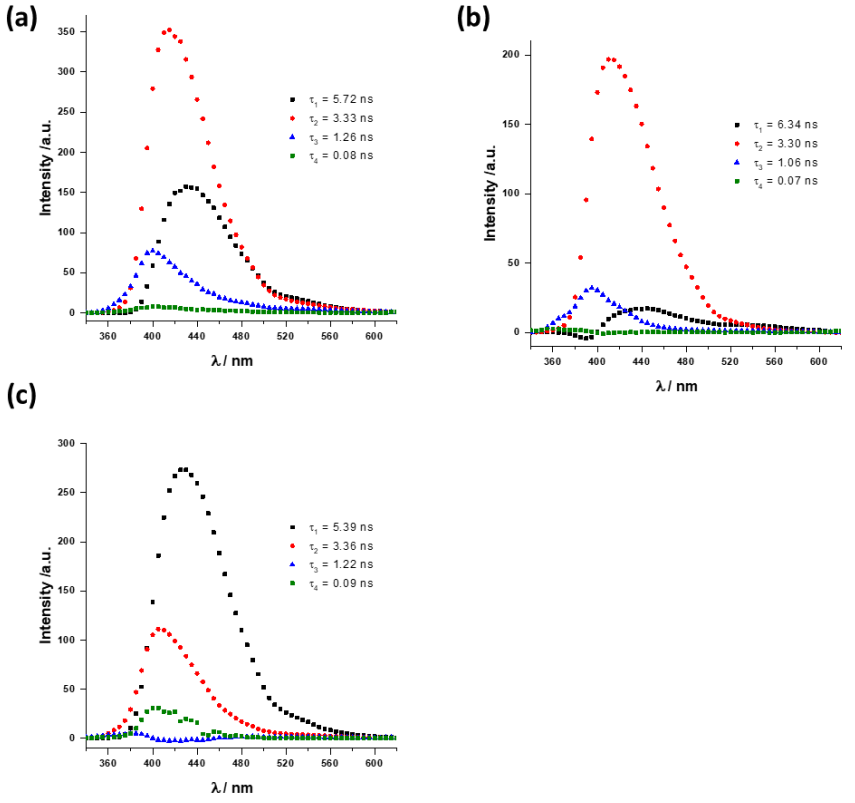


Figure S108. SAEMS spectra of compound (*S,S,P*)-**5** in (a) CH_2Cl_2, (b) hexane, (c) MeOH.

5. PHOTOPHYSICAL PROPERTIES

Experimental Conditions

Both absorption and emission measurements were performed in an Olis DSM172 spectrophotometer using a 1.0 cm path-length quartz cell and 2.5×10^{-5} M solutions of the ligands in HPLC grade solvents. A xenon lamp of 150 W was used for absorption measurements, while to emission measurements fixed wavelength LED (300 nm) was used as the excitation source.

Absorbance and CD spectra of (*S*,*S*,*P*)-**7**:Pd(II) and (*R*,*R*,*M*)-**7**:Pd(II) were recorded from 1.8×10^{-3} M solutions in CD_2Cl_2 using a 0.1 mm quartz cell (Hellma 0.1 mm quartz Suprasil®). Full coordination of the ligand and complete formation of the complexes was checked by ^{1}H NMR both before and after the study of the photophysical properties of the system (Figures S124 and S125).

Absorbance and steady-state fluorescence spectra

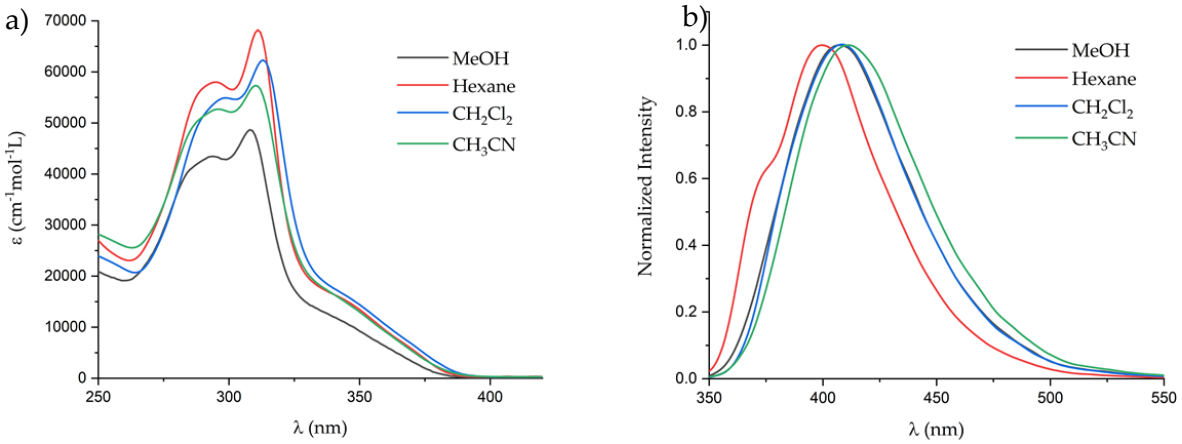


Figure S109. a) Absorption and b) fluorescence emission (λ_{exc} = 300 nm) spectra of compound (*S*,*S*,*P*)-**1** in different solvents

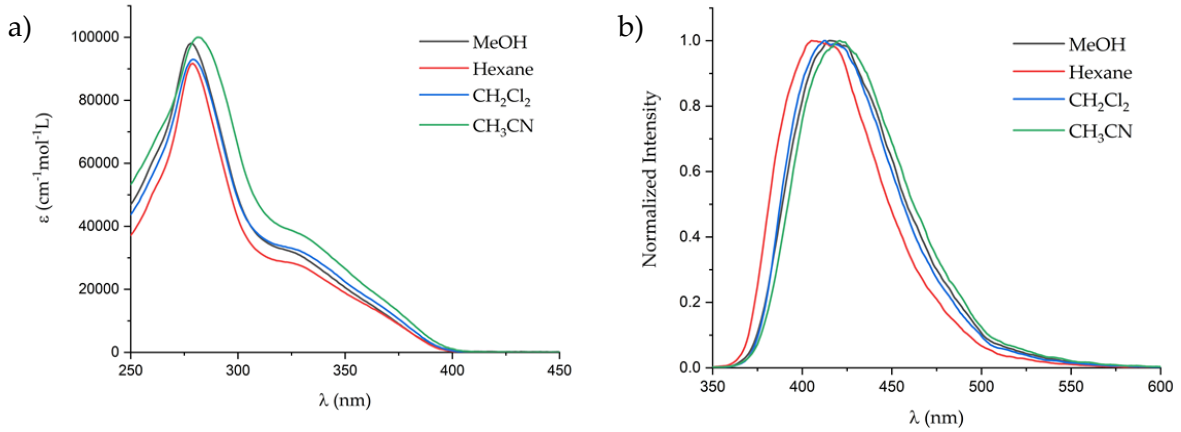


Figure S110. a) Absorption and b) fluorescence emission (λ_{exc} = 300 nm) spectra of compound (*S*,*S*,*P*)-**2** in different solvents

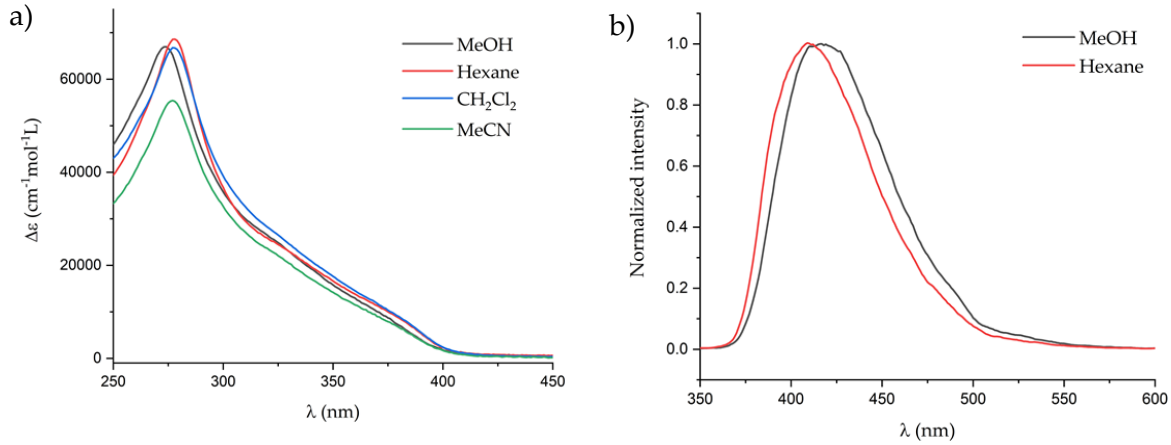


Figure S111. a) Absorption and b) fluorescence emission (λ_{exc} = 300 nm) spectra of compound (*S*,*S*,*P*)-**3** in different solvents

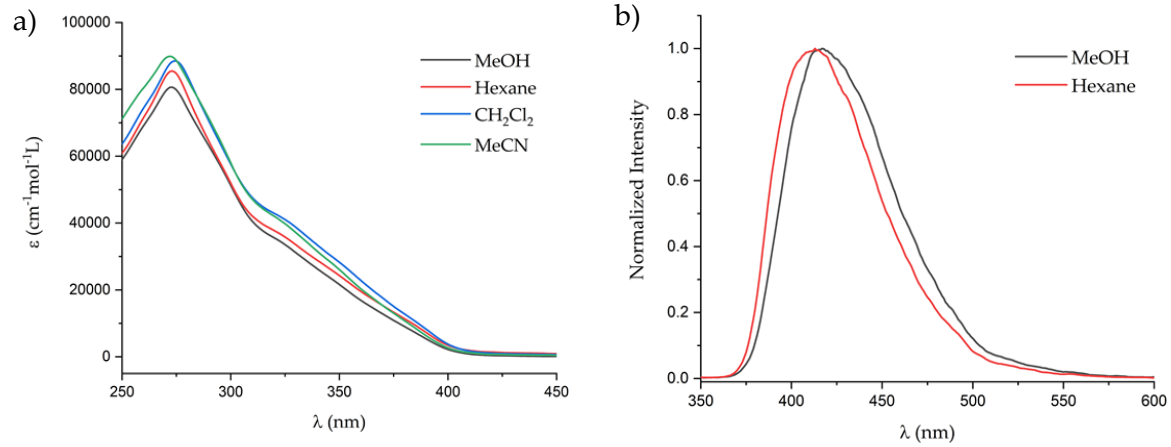


Figure S112. a) Absorption and b) fluorescence emission (λ_{exc} = 300 nm) spectra of compound (*S*,*S*,*P*)-**4** in different solvents

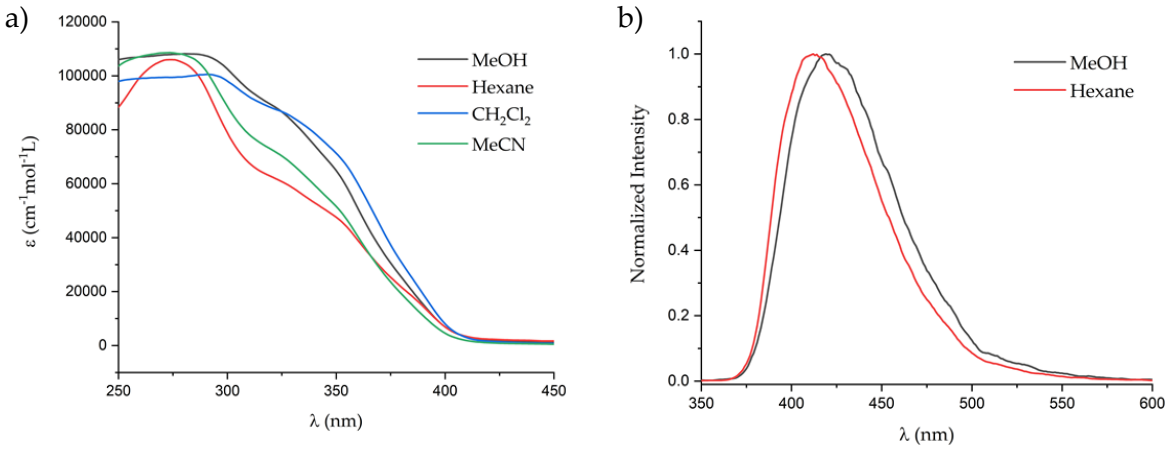


Figure S113. a) Absorption and b) fluorescence emission (λ_{exc} = 300 nm) spectra of compound (*S*,*S*,*P*)-**5** in different solvents

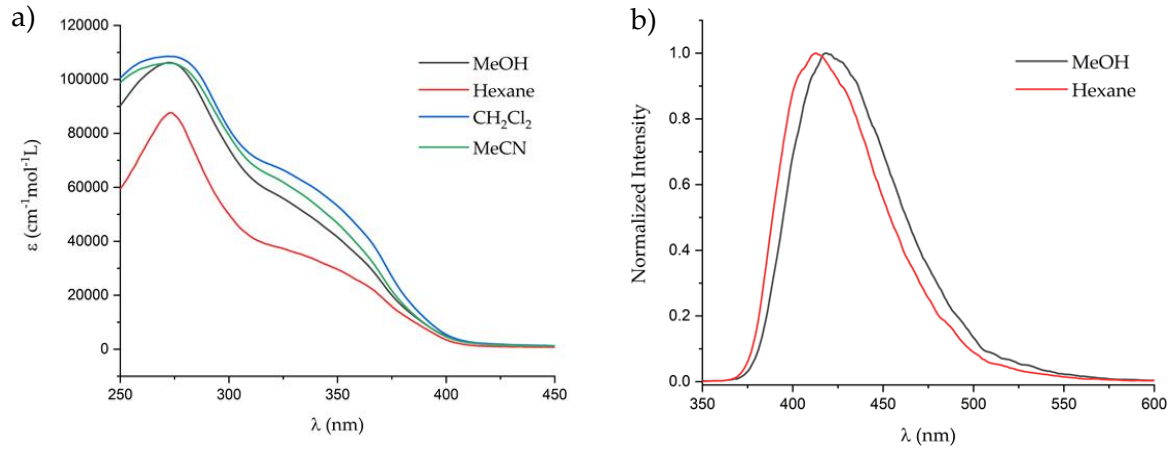


Figure S114. a) Absorption and b) fluorescence emission (λ_{exc} = 300 nm) spectra of compound (*S*,*S*,*P*)-**6** in different solvents

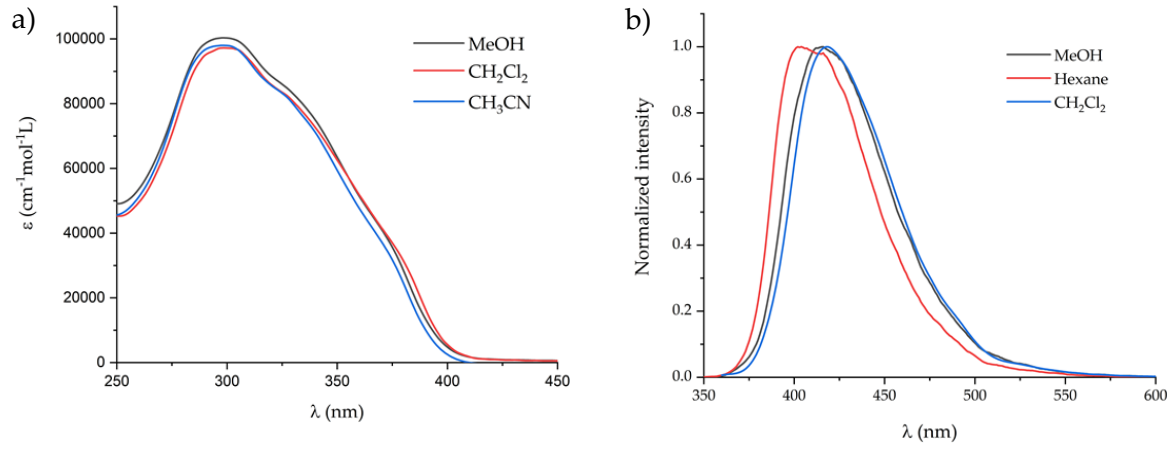


Figure S115. a) Absorption and b) fluorescence emission (λ_{exc} = 300 nm) spectra of compound (*S*,*S*,*P*)-**7** in different solvents.

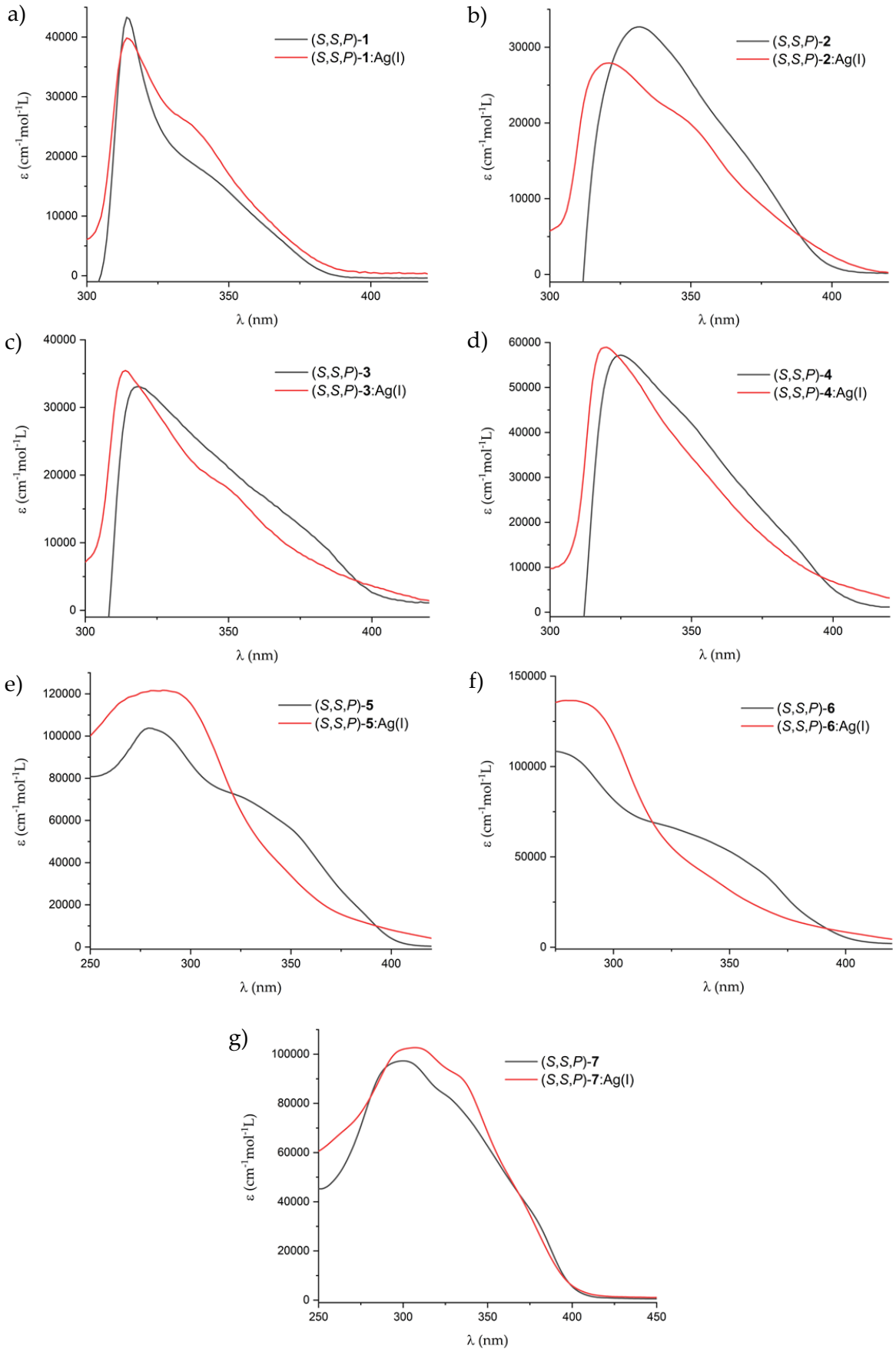

a)
(S,S,P)-1
(S,S,P)-1:Ag(I)
ε (cm-1mol-1L)
λ (nm)
b)
(S,S,P)-2
(S,S,P)-2:Ag(I)
ε (cm-1mol-1L)
λ (nm)
c)
(S,S,P)-3
(S,S,P)-3:Ag(I)
ε (cm-1mol-1L)
λ (nm)
d)
(S,S,P)-4
(S,S,P)-4:Ag(I)
ε (cm-1mol-1L)
λ (nm)
e)
(S,S,P)-5
(S,S,P)-5:Ag(I)
ε (cm-1mol-1L)
λ (nm)
f)
(S,S,P)-6
(S,S,P)-6:Ag(I)
ε (cm-1mol-1L)
λ (nm)
g)
(S,S,P)-7
(S,S,P)-7:Ag(I)
ε (cm-1mol-1L)
λ (nm)

Figure S116. Absorption spectra of compounds a) (*S*,*S*,*P*)-**1**, b) (*S*,*S*,*P*)-**2**, c) (*S*,*S*,*P*)-**3**, d) (*S*,*S*,*P*)-**4**, e) (*S*,*S*,*P*)-**5**, f) (*S*,*S*,*P*)-**6**, g) (*S*,*S*,*P*)-**7** in 9:1 mixtures of CH_2Cl_2:Acetone in absence (black line) and presence (red line) of $AgBF_4$.

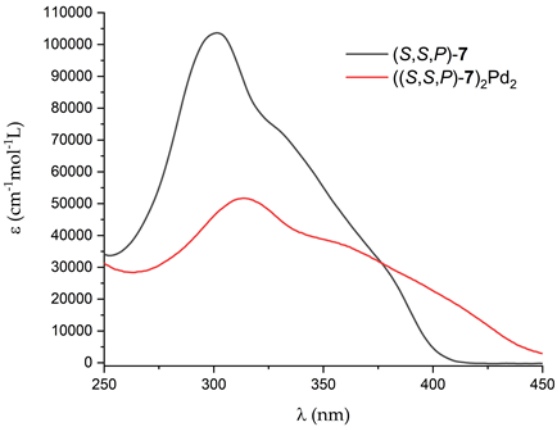


Figure S117. Absorption spectra of compound (*S*,*S*,*P*)-**7** in CH_2Cl_2 in absence (black line) and presence (red line) of $Pd(CH_3CN)_2Cl_2$.

CD measurements of (S,S,P)-1-7 in different solvents

CD spectra of (*S*,*S*,*P*)-**1-7** were collected by accumulating 30 scans.

In all the cases a fixed slit-width of 1 mm and 0.1s of integration time were selected.

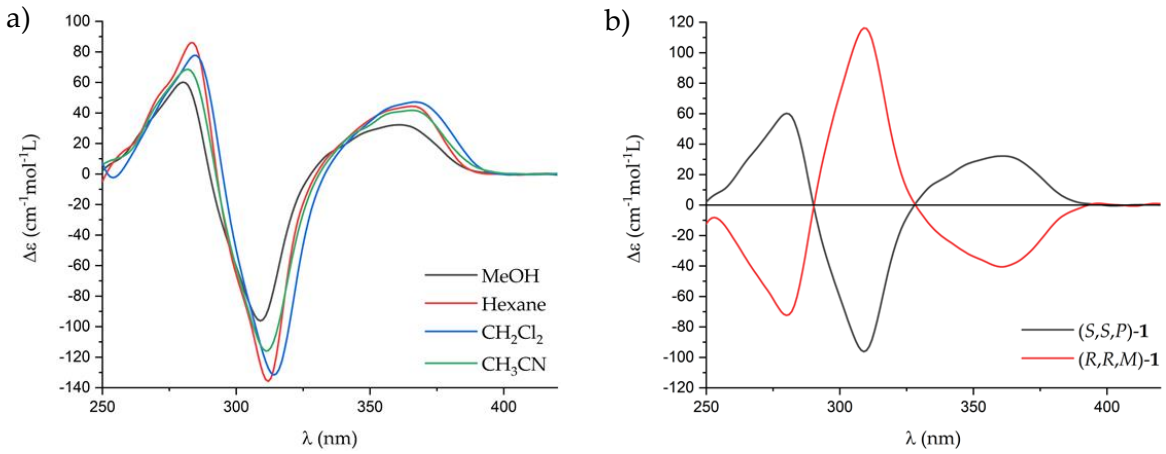


Figure S118. CD spectra of compound a) (*S*,*S*,*P*)-**1** in MeOH (black line), hexane (red line), CH_2Cl_2 (blue line) and CH_3CN (green line), b) (*S*,*S*,*P*)-**1** (black line) and (*R*,*R*,*M*)-**1** (red line) in MeOH.

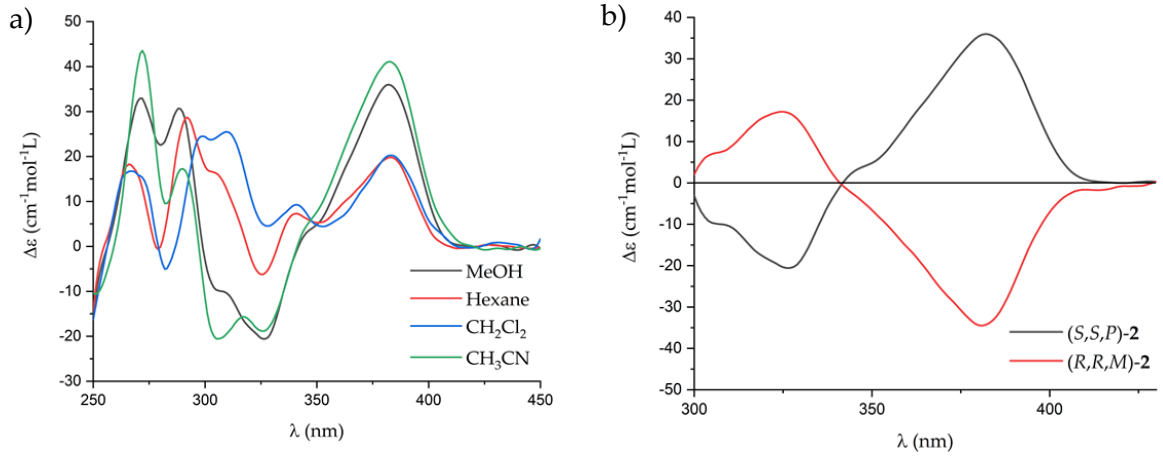


Figure S119. CD spectra of compound a) (*S*,*S*,*P*)-**2** in MeOH (black line), hexane (red line), CH_2Cl_2 (blue line) and CH_3CN (green line), b) (*S*,*S*,*P*)-**2** (black line) and (*R*,*R*,*M*)-**2** (red line) in MeOH.

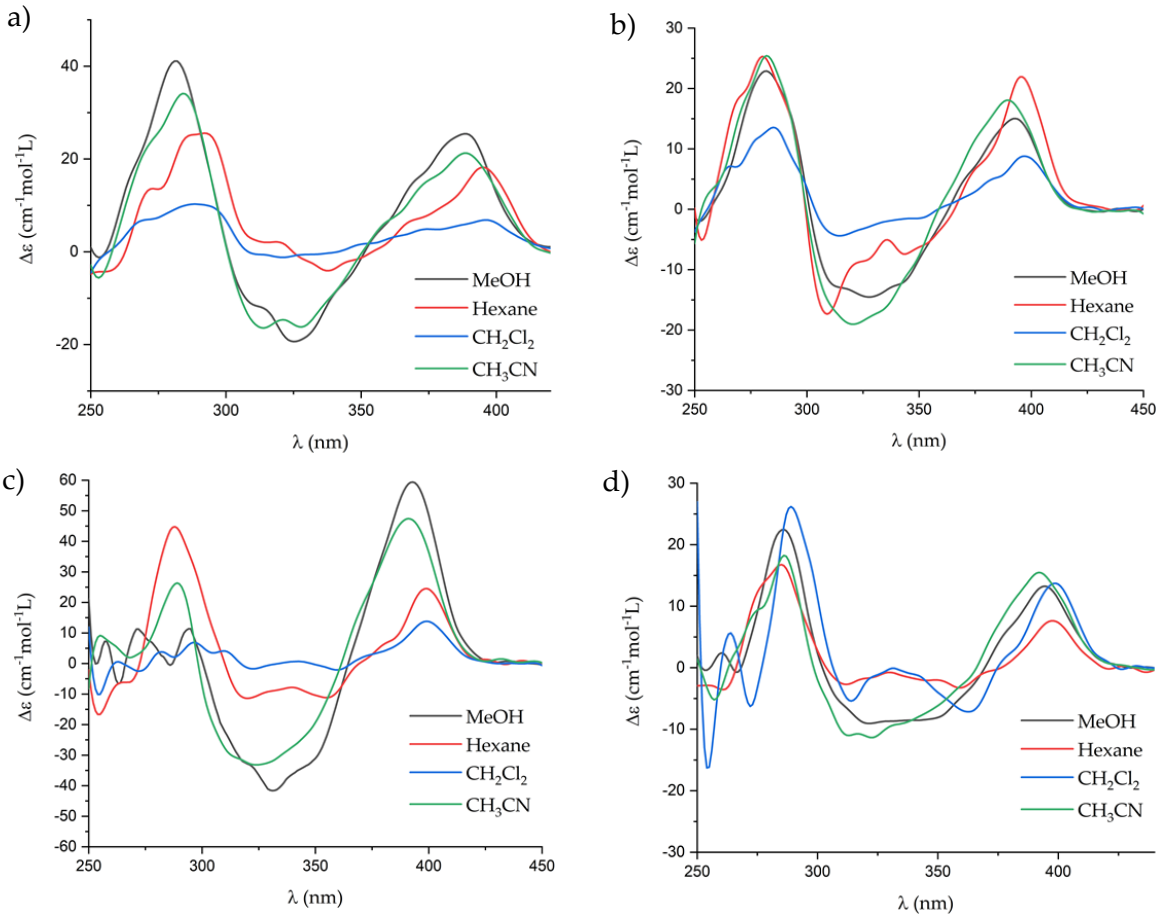


Figure S120. CD spectra of compounds a) (*S*,*S*,*P*)-**3** b) (*S*,*S*,*P*)-**4** c) (*S*,*S*,*P*)-**5** d) (*S*,*S*,*P*)-**6** in MeOH (black line), hexane (red line), CH_2Cl_2 (blue line) and CH_3CN (green line).

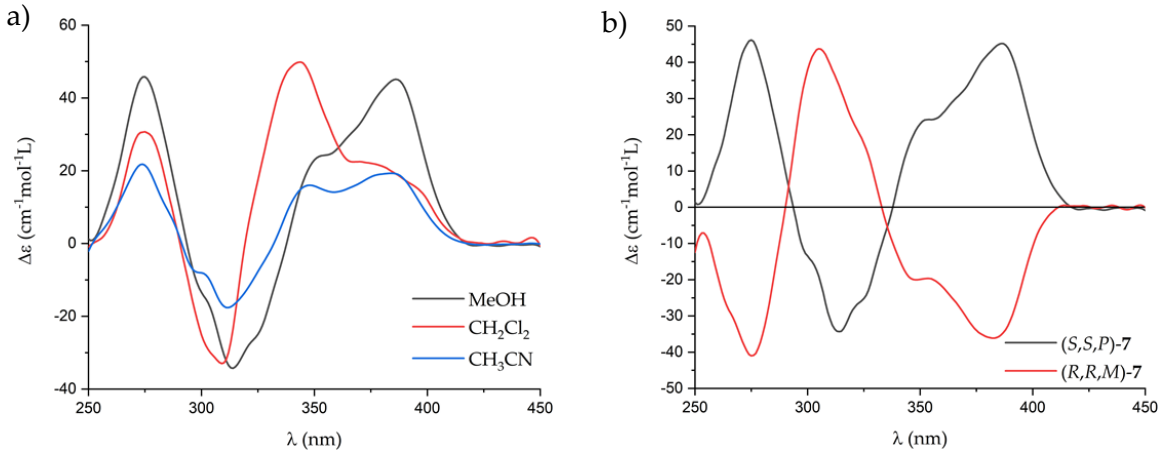


Figure S121. CD spectra of compound a) (*S*,*S*,*P*)-**7** in MeOH (black line), CH_2Cl_2 (red line) and CH_3CN (blue line), b) (*S*,*S*,*P*)-**7** (black line) and (*R*,*R*,*M*)-**7** (red line) in MeOH.

Table S6. g_{abs} values of (*S*,*S*,*P*)-**1**-**7** in different solvents.

g_{abs}	CH_2Cl_2	*MeOH*	*Hexane*	*MeCN*
(*S*,*S*,*P*)-***1***	1×10^{-2} (387nm)	1.3×10^{-2} (384nm)	0.9×10^{-2} (380nm)	1×10^{-2} (385nm)
(*S*,*S*,*P*)-***2***	0.8×10^{-2} (395nm)	1.4×10^{-2} (395nm)	1×10^{-2} (395nm)	1×10^{-2} (395nm)
(*S*,*S*,*P*)-***3***	0.3×10^{-2} (405nm)	0.8×10^{-2} (393nm)	0.8×10^{-2} (403nm)	0.9×10^{-2} (403nm)
(*S*,*S*,*P*)-***4***	0.3×10^{-2} (403nm)	0.6×10^{-2} (400nm)	0.6×10^{-2} (403nm)	0.5×10^{-2} (402nm)
(*S*,*S*,*P*)-***5***	0.3×10^{-2} (410nm)	0.7×10^{-2} (404nm)	0.4×10^{-2} (409nm)	0.9×10^{-2} (401nm)
(*S*,*S*,*P*)-***6***	0.3×10^{-2} (407nm)	0.2×10^{-2} (401nm)	0.3×10^{-2} (404nm)	0.3×10^{-2} (405nm)
(*S*,*S*,*P*)-***7***	0.3×10^{-2} (410nm)	0.4×10^{-2} (402nm)	Insoluble	0.8×10^{-2} (406nm)

CD measurements of formed complexes

CD spectra of (*S*,*S*,*P*)-**1-7**:Ag(I) were collected by accumulating 30 scans, while CD spectra of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$ and ((*R*,*R*,*M*)-**7**)$_2$Pd$_2$ were collected by accumulating 50 scans.

In all the cases a fixed slit-width of 1 mm and 0.1s of integration time were selected.

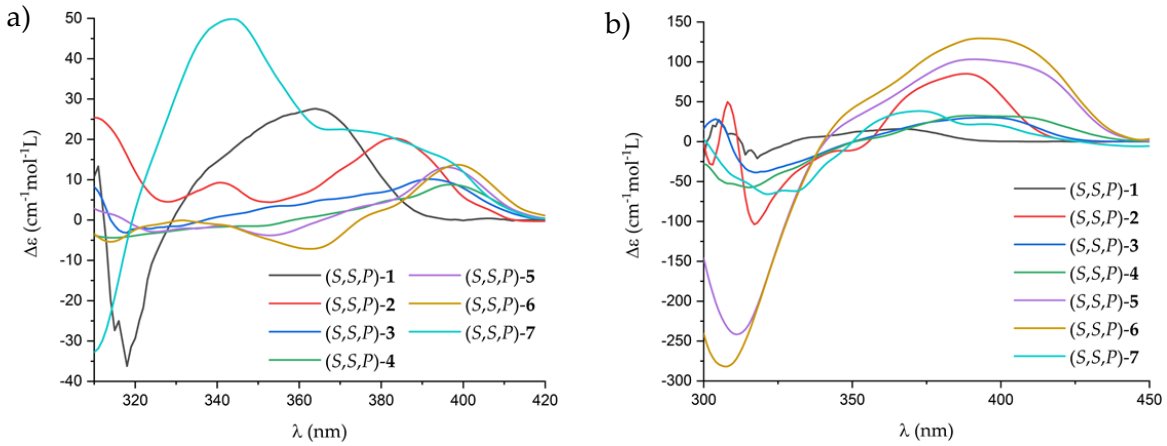


Figure S122. CD spectra of compounds (*S,S,P*)-**1-7** in 9:1 mixtures of CH_2Cl_2:Acetone in a) absence and b) presence of $AgBF_4$.

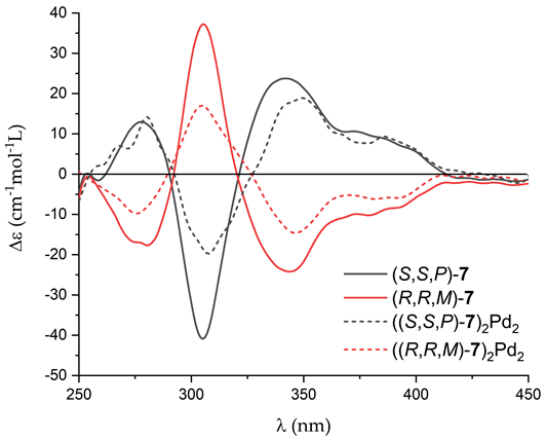


Figure S123. CD spectra of compounds (*S,S,P*)-**7** and (*R,R,M*)-**7** in CH_2Cl_2 (1.8 mM) in absence and presence of $Pd(CH_3CN)_2Cl_2$.

Table S7. g_{abs} values of (*S,S,P*)-**1-7**:Ag(I) and ((*S,S,P*)-**7**)$_2Pd_2$ in different solvents.

g_{abs}	CH_2Cl_2:Acetone
(*S,S,P*)-***1***:*Ag(I)*	0.9×10^{-2} (401nm)
(*S,S,P*)-***2***:*Ag(I)*	2.5×10^{-2} (402nm)
(*S,S,P*)-***3***:*Ag(I)*	1×10^{-2} (409nm)
(*S,S,P*)-***4***:*Ag(I)*	0.6×10^{-2} (419nm)
(*S,S,P*)-***5***:*Ag(I)*	1.7×10^{-2} (419nm)
(*S,S,P*)-***6***:*Ag(I)*	2.2×10^{-2} (418nm)
(*S,S,P*)-***7***:*Ag(I)*	0.4×10^{-2} (402nm)
((*S,S,P*)-***7***)$_2$*Pd*$_2$	0.1×10^{-2} (401nm)

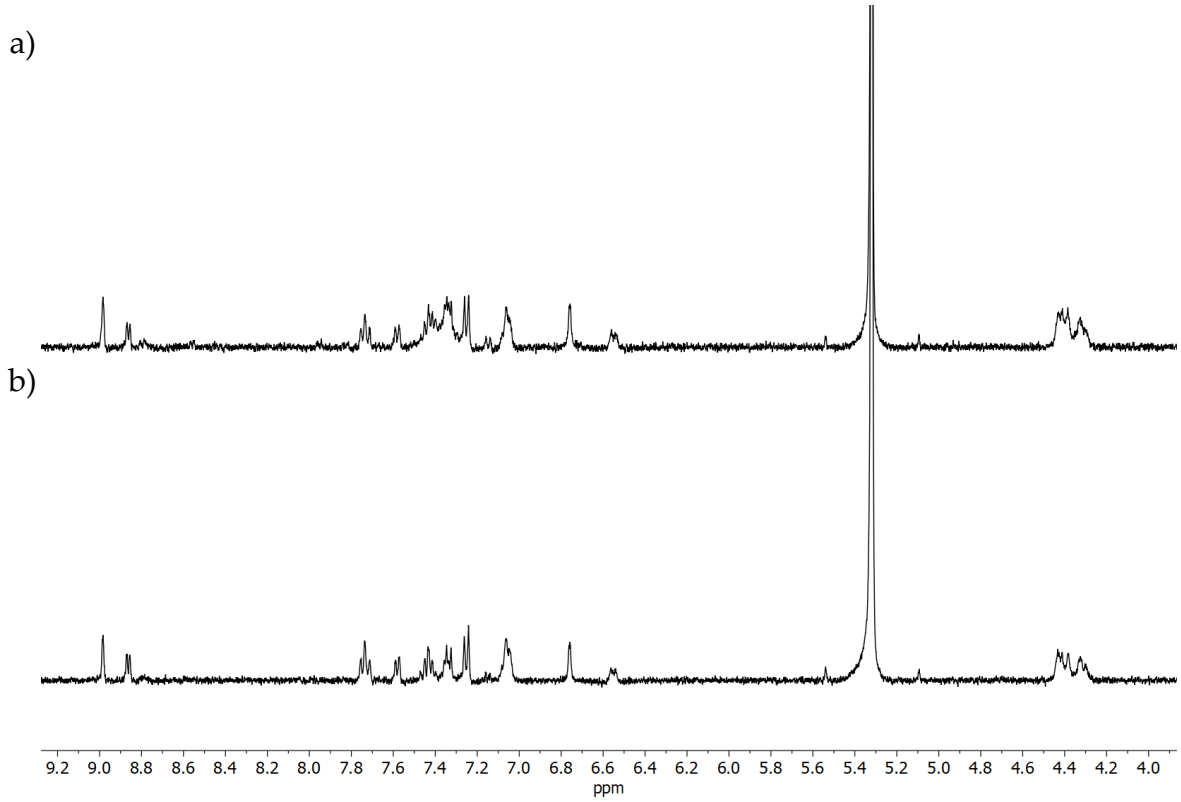


Figure S124. a) Previous and b) subsequent ^{1}H NMR realized to the study of the photophysical properties of the ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$.

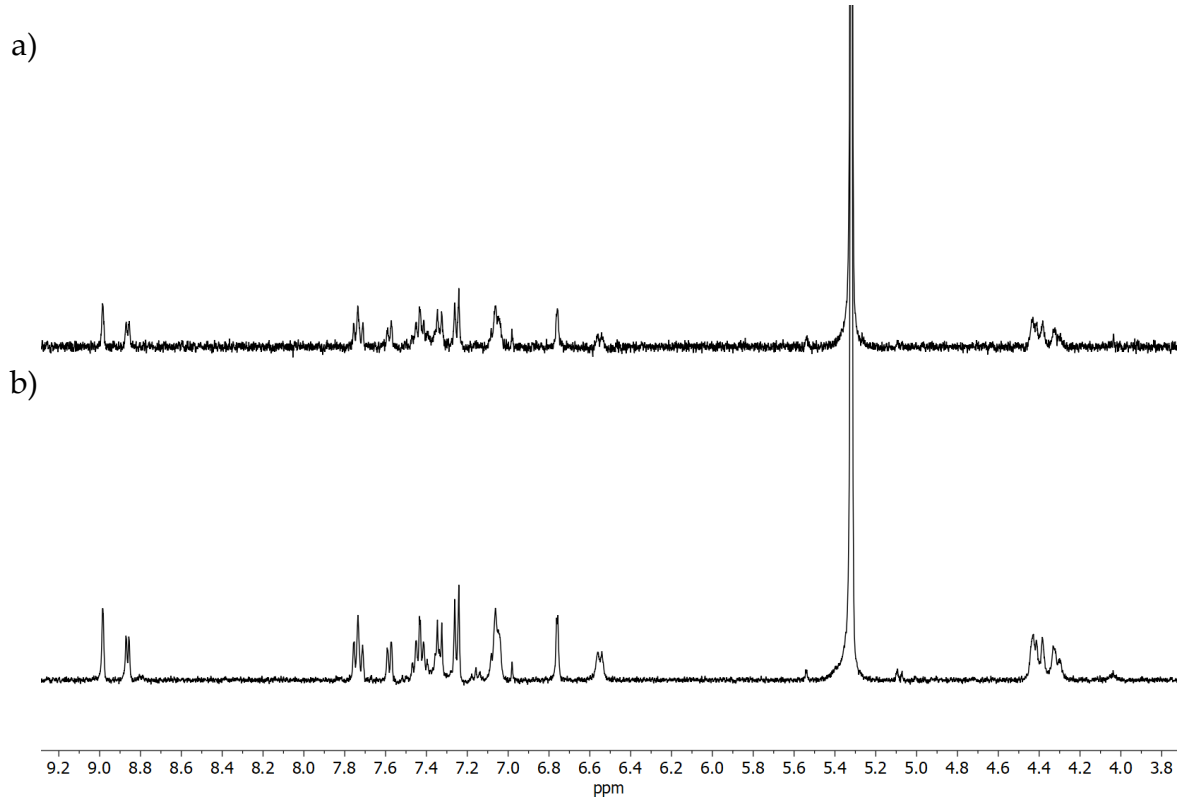


Figure S125. a) Previous and b) subsequent ^{1}H NMR realized to the study of the photophysical properties of the ((*R*,*R*,*M*)-**7**)$_2$Pd$_2$.

CD Titration of compounds (S,S,P)-1-7 with $AgBF_4$

Titrations of compounds (*S*,*S*,*P*)-**N** (**N=1-7**) were carried out by addition of progressive quantities of a solution of $AgBF_4$ (2.5×10^{-4}M), which was commercially available, to a solution of the corresponding compound in 9:1 mixture of CH_2Cl_2:acetone (2.5×10^{-5}M) (some drops of methanol were added in the cases that salts were not soluble at all). To make the fitting of the kinetic constant easier, concentration of ligands (*S*,*S*,*P*)-**N** was kept constant during the titration. To ensure this, 2.5×10^{-5}M solution of these compounds was used as solvent to prepare the metal solution. The fitting was carried out with BindFit online program (v. 0.5), using the Globalized Bounded Nelder–Mead (GBNM) method.[11]

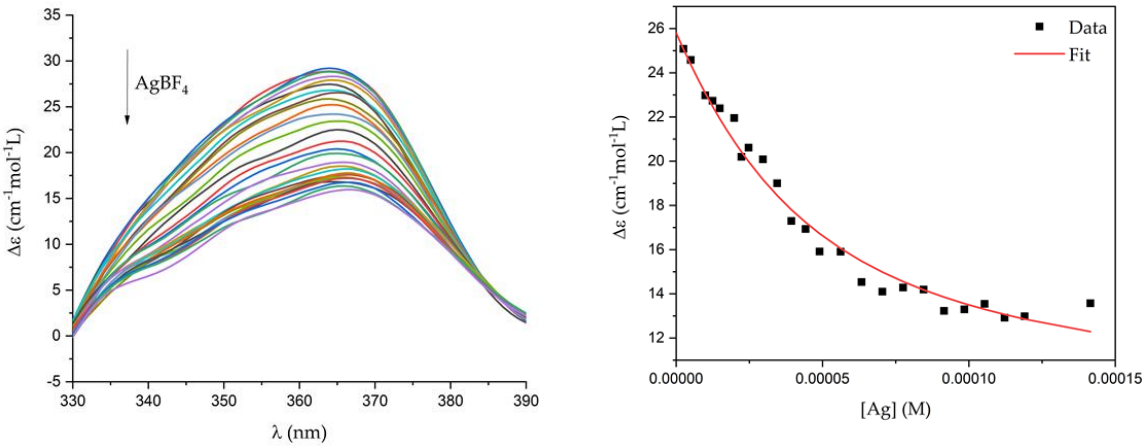


Figure S126. CD titration of compound (*S*,*S*,*P*)-**1** with $AgBF_4$. Fitting of the changes in CD for the signal at 359 nm. K = 3.25 x10^4± 0.07 x10^4 M^{-1}

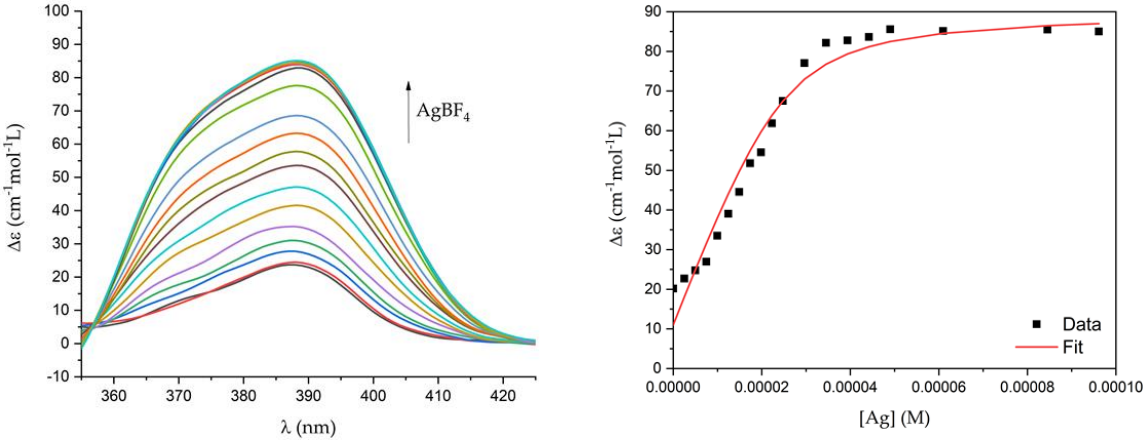


Figure S127. CD titration of compound (*S*,*S*,*P*)-**2** with $AgBF_4$. Fitting of the changes in CD for the signal at 379 nm. K = 3.7 x10^5 ± 0.2 x10^5 M^{-1}

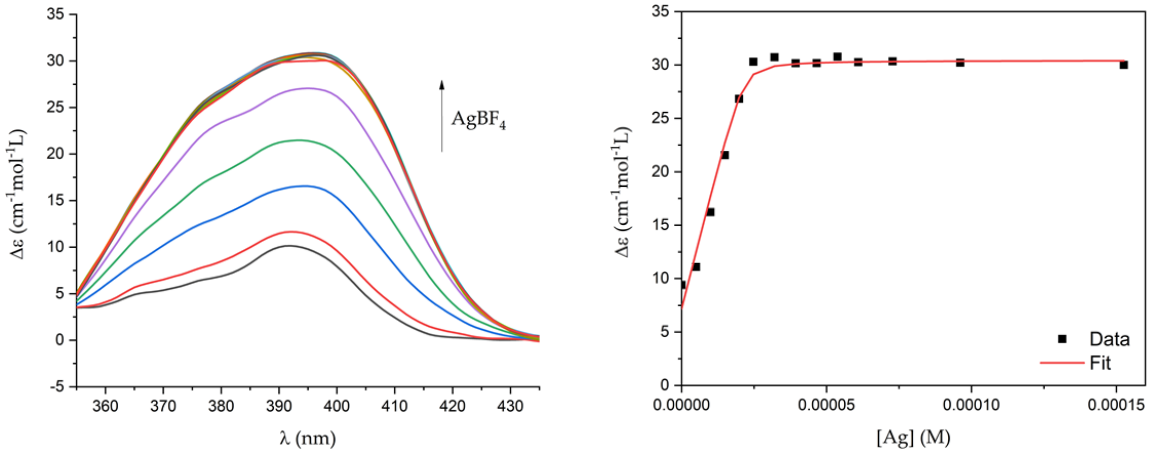


Figure S128. CD titration of compound (*S*,*S*,*P*)-**3** with $AgBF_4$. Fitting of the changes in CD for the signal at 379 nm. K = 3.7 x10^6 ± 0.56 x10^6 M^{-1}

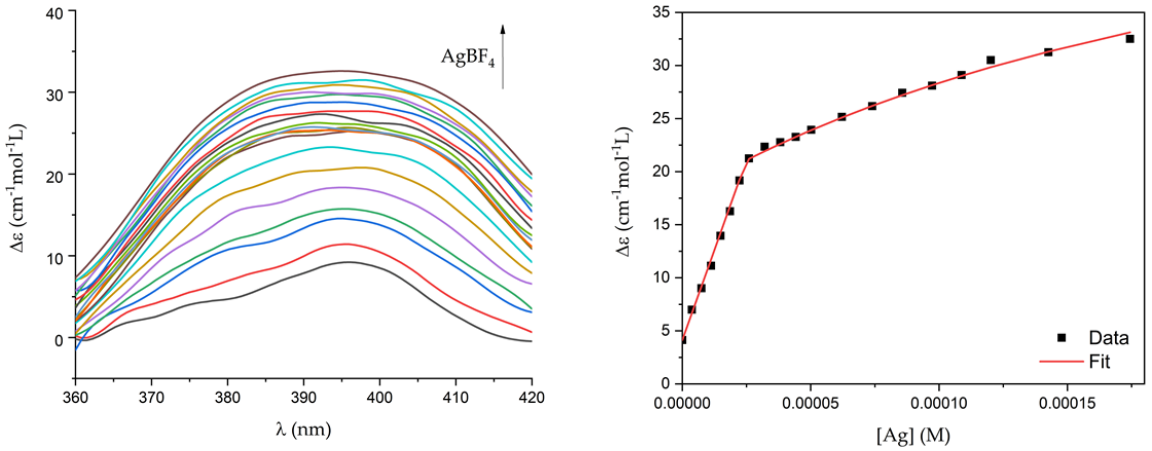


Figure S129. CD titration of compound (*S*,*S*,*P*)-**4** with $AgBF_4$. Fitting of the changes in CD for the signal at 379 nm. K_{11+12} = 24x10^9 ± 2.9x10^9 M^{-2}

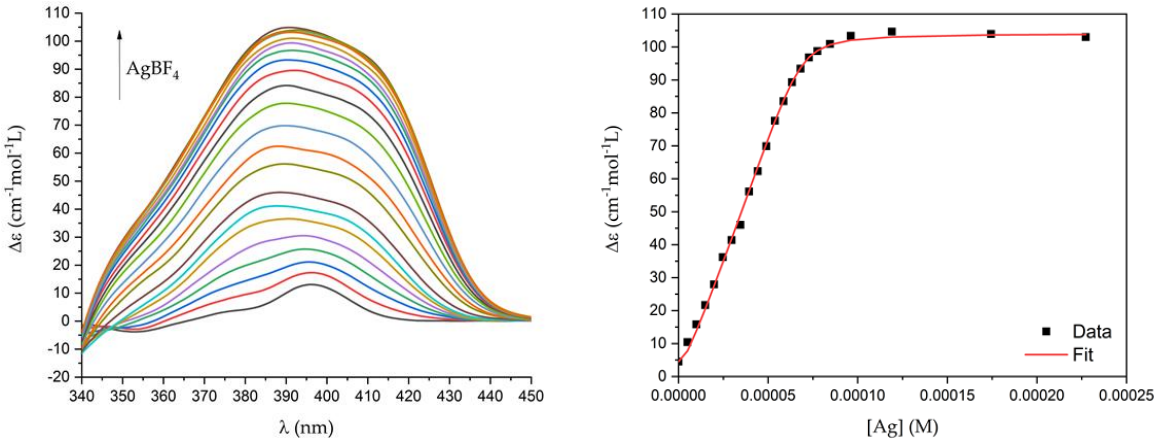


Figure S130. CD titration of compound (*S*,*S*,*P*)-**5** with $AgBF_4$. Fitting of the changes in CD for the signal at 379 nm. K_{11+12} = 1.8 x10^{10} ± 0.03 x10^{10} M^{-2}

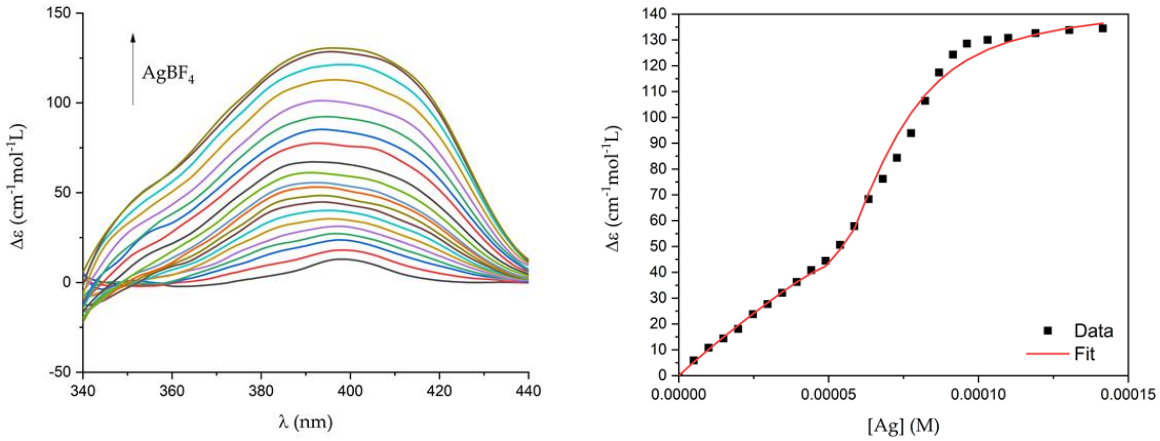


Figure S131. CD titration of compound (*S,S,P*)-**6** with $AgBF_4$. Fitting of the changes in CD for the signal at 379 nm. $K_{11+12+13} = 27 \times 10^{16} \pm 5.3 \times 10^{16}\ M^{-3}$

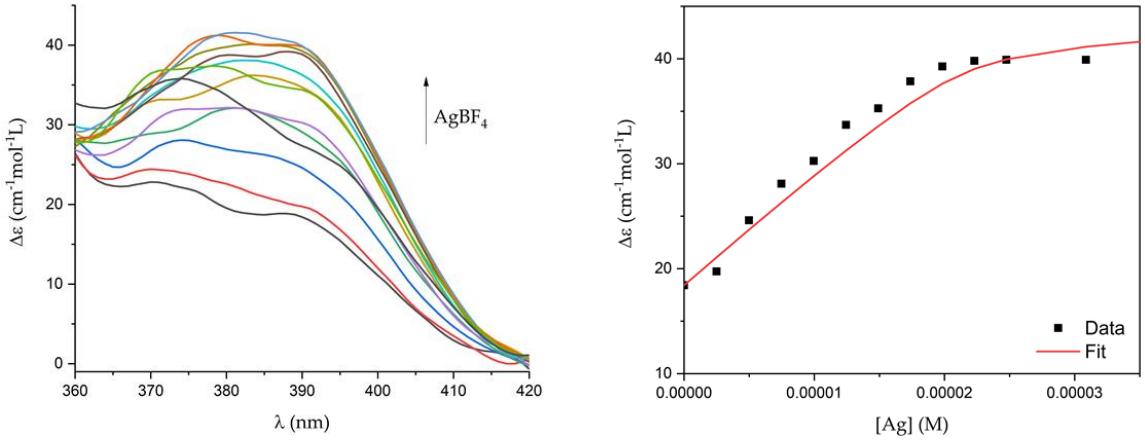


Figure S132. CD titration of compound (*S,S,P*)-**7** with $AgBF_4$. Fitting of the changes in CD for the signal at 390 nm. $K = 8.2 \times 10^5\ M^{-1} \pm 1.1 \times 10^5\ M^{-1}$

CPL measurements of (S,S,P)-1-7 in different solvents

CPL spectra of compounds **1-7** were collected by accumulating 70 scans.
In all the cases a 1 s of integration time were selected.

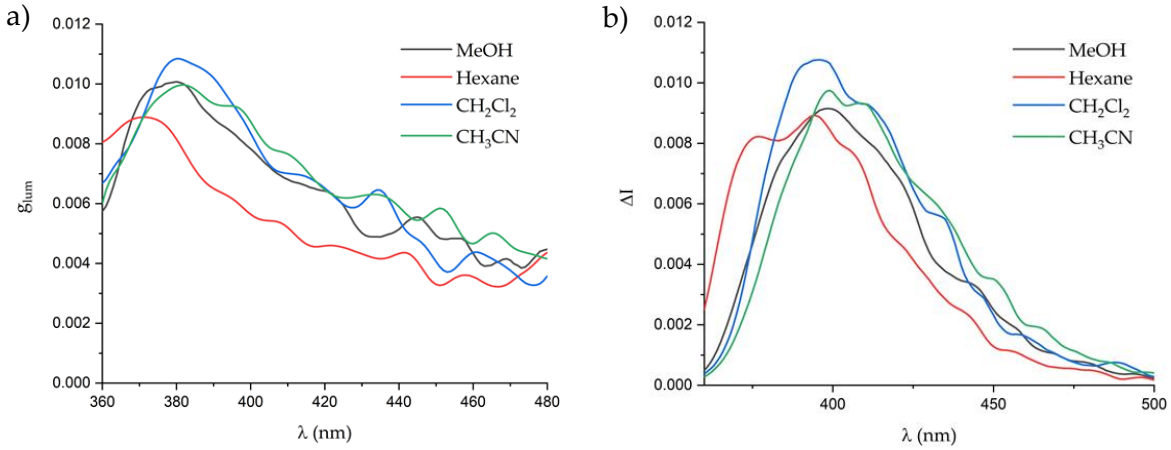


Figure S133. a) glum and b) ΔI values obtained for compound (*S*,*S*,*P*)-**1** in MeOH (black line), hexane (red line), CH_2Cl_2 (blue line) and CH_3CN (green line)

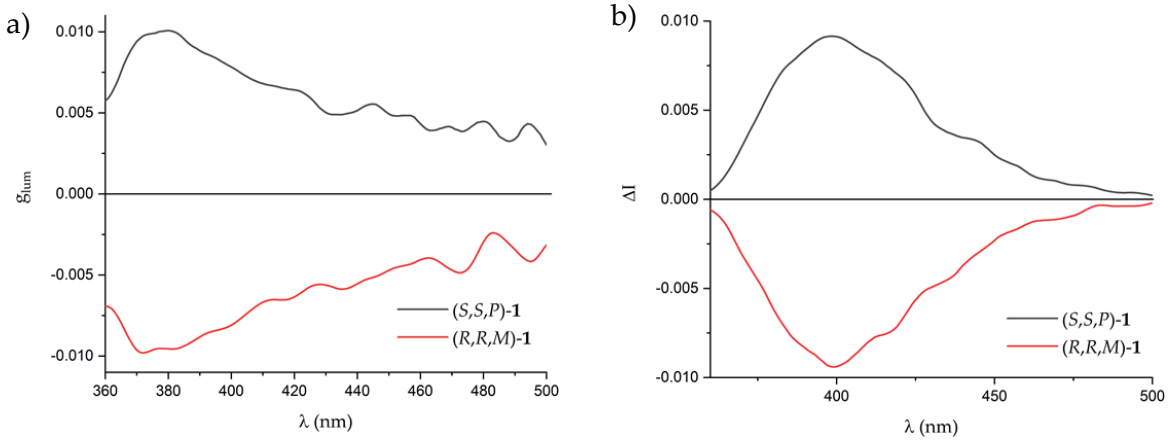


Figure S134. a) glum and b) ΔI values obtained for compound (*S*,*S*,*P*)-**1** (black line) and (*R*,*R*,*M*)-**1** (red line) in MeOH.

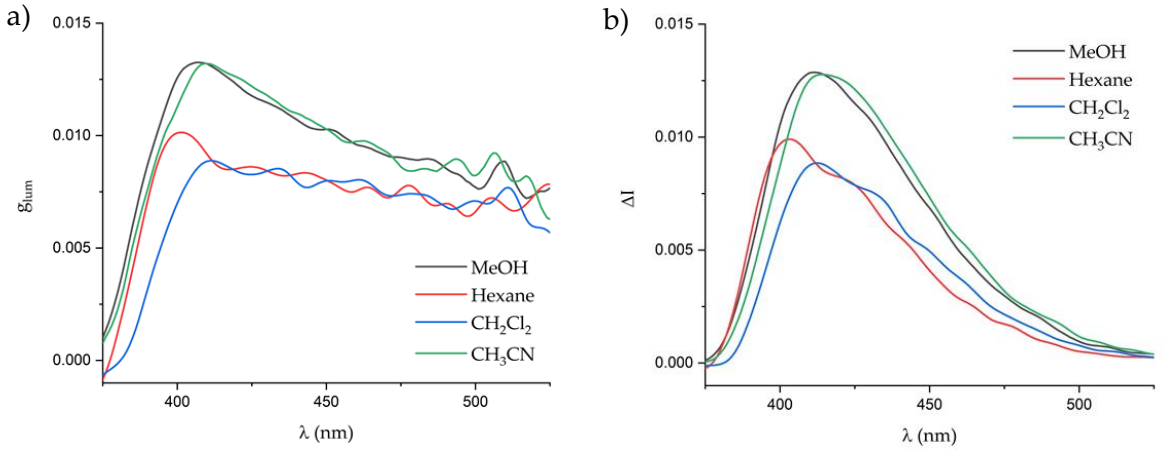


Figure S135. a) glum and b) ΔI values obtained for compound (*S*,*S*,*P*)-**2** in MeOH (black line), hexane (red line), CH_2Cl_2 (blue line) and CH_3CN (green line)

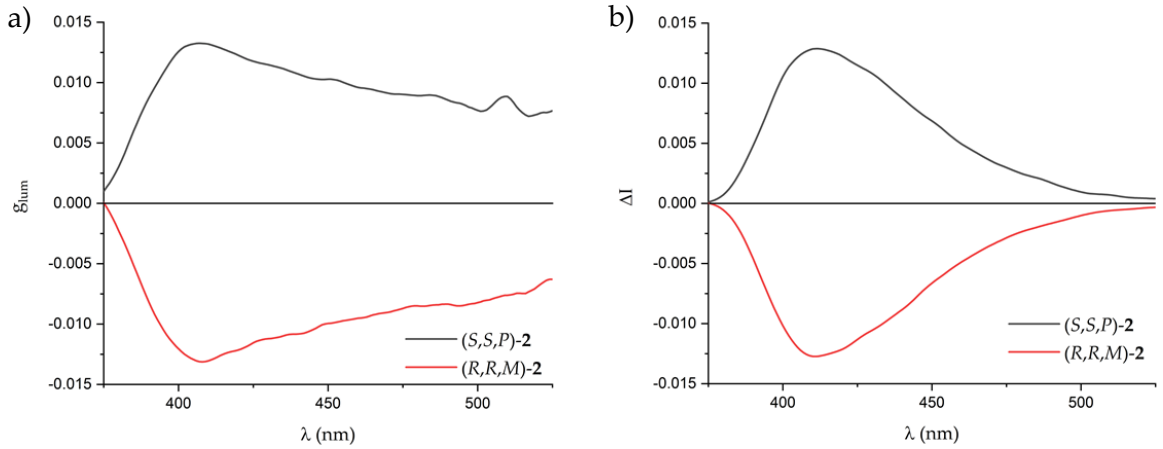


Figure S136. a) glum and b) ΔI values obtained for compound (*S,S,P*)-**2** (black line) and (*R,R,M*)-**2** (red line) in MeOH.

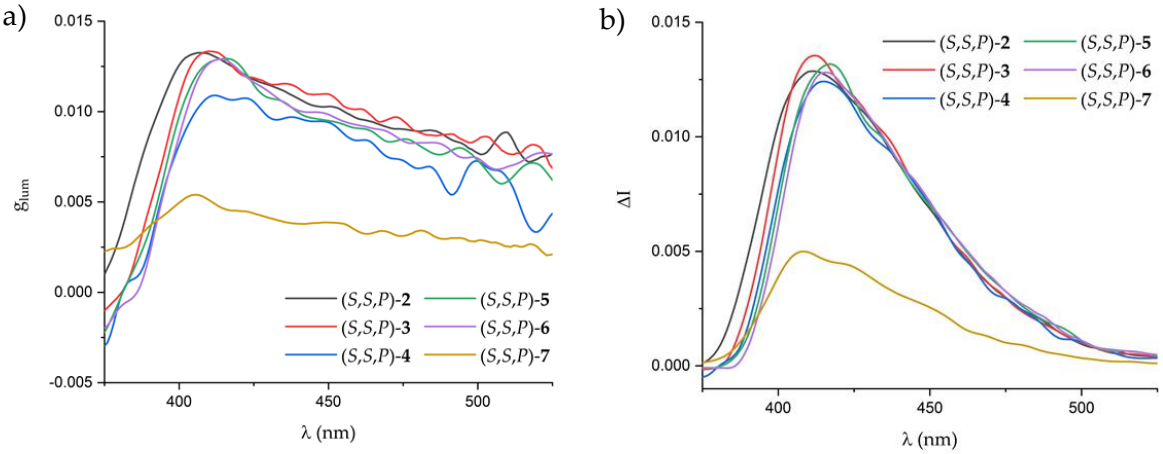


Figure S137. a) g_{lum} and b) ΔI values obtained for compounds (*S,S,P*)-**2-7** in MeOH.

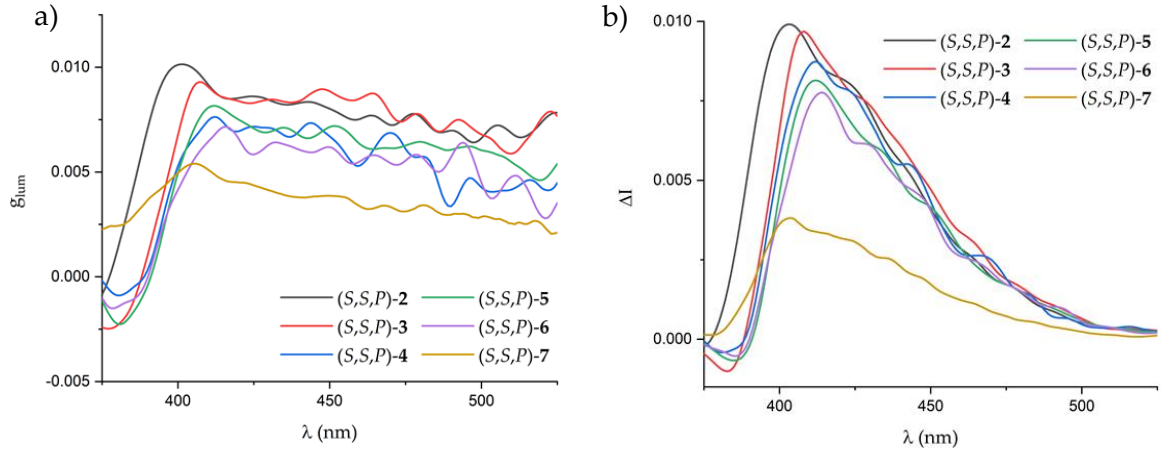


Figure S138. a) g_{lum} and b) ΔI values obtained for compounds (*S,S,P*)-**2-7** in Hexane.

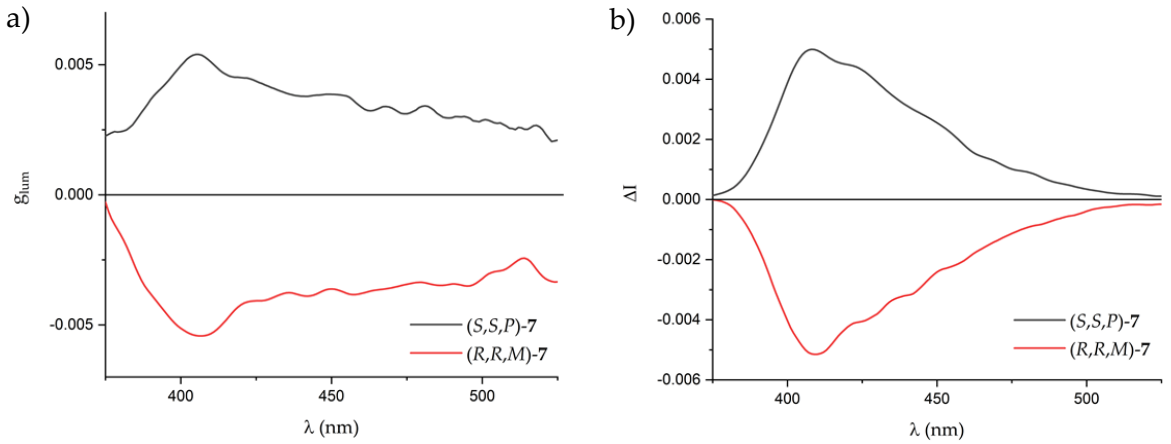


Figure S139. a) g_{lum} and b) ΔI values obtained for compound (*S,S,P*)-**7** (black line) and (*R,R,M*)-**7** (red line) in MeOH.

Table S8. g_{lum} values to (*S,S,P*)-**1**-**7** in different solvents.

glum	*CH_2Cl_2*	*MeOH*	*Hexane*	*MeCN*
(*S,S,P*)-***1***	1.1 × 10^{-2} (380nm)	1 × 10^{-2} (380nm)	0.9 × 10^{-2} (371nm)	1 × 10^{-2} (382nm)
(*S,S,P*)-***2***	0.9 × 10^{-2} (411nm)	1.3 × 10^{-2} (407nm)	1 × 10^{-2} (401nm)	1.3 × 10^{-2} (410nm)
(*S,S,P*)-***3***		1.3 × 10^{-2} (408nm)	0.9 × 10^{-2} (410nm)	
(*S,S,P*)-***4***		1.1 × 10^{-2} (412nm)	0.7 × 10^{-2} (412nm)	
(*S,S,P*)-***5***		1.3 × 10^{-2} (416nm)	0.8 × 10^{-2} (412nm)	
(*S,S,P*)-***6***		1.3 × 10^{-2} (414nm)	0.7 × 10^{-2} (416nm)	
(*S,S,P*)-***7***		0.5 × 10^{-2} (405nm)	Insoluble	

6. EXPERIMENTAL IR AND VCD MEASUREMENTS

IR and VCD spectra have been recorded in CD_2Cl_2 solutions, ranging from 0.01 to 0.018M concentration. One, two, three equivalent of $AgBF_4$ salt have been added to the original solution. A 500 mm BaF_2 cell has been used. Measurements have been undertaken with a Jasco FVS6000 FTIR spectrometer equipped with a VCD module, comprised of a wire-grid linear polarizer, a ZnSe Photo Elastic Modulator to produce 50 kHz modulated circularly polarized radiation and a liquid N2-cooled MCT detector. In all cases, IR and VCD spectra have been solvent subtracted.

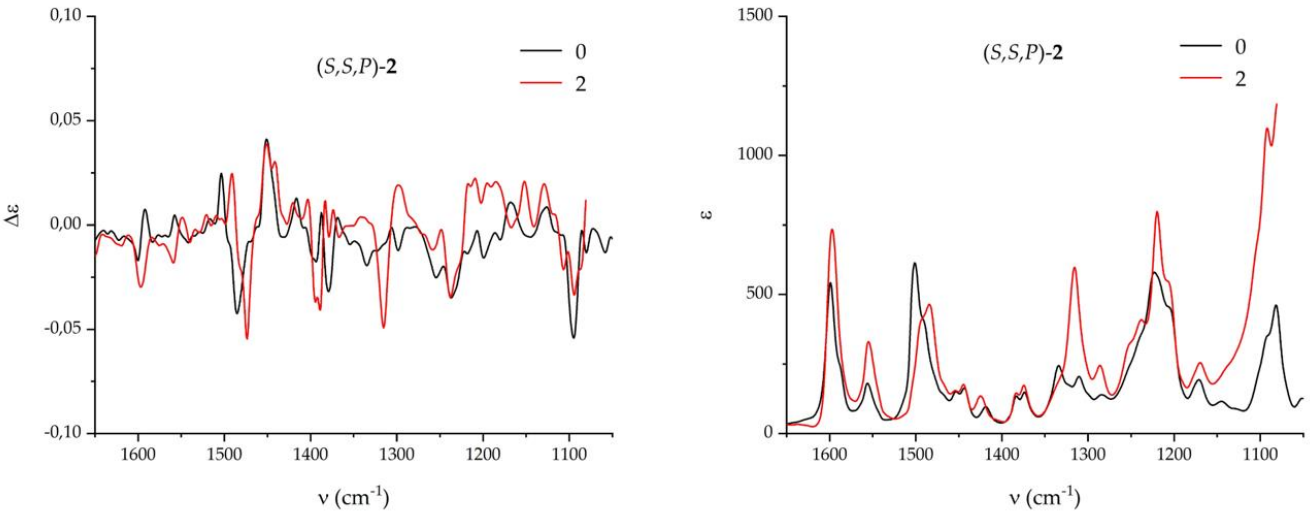


Figure S140. VCD (left) and IR (right) spectra for the compound (*S*,*S*,*P*)-**2** in CH_2Cl_2 solution and after addition of $AgBF_4$ salt (salt: compound molarity ratios are indicated by labels).

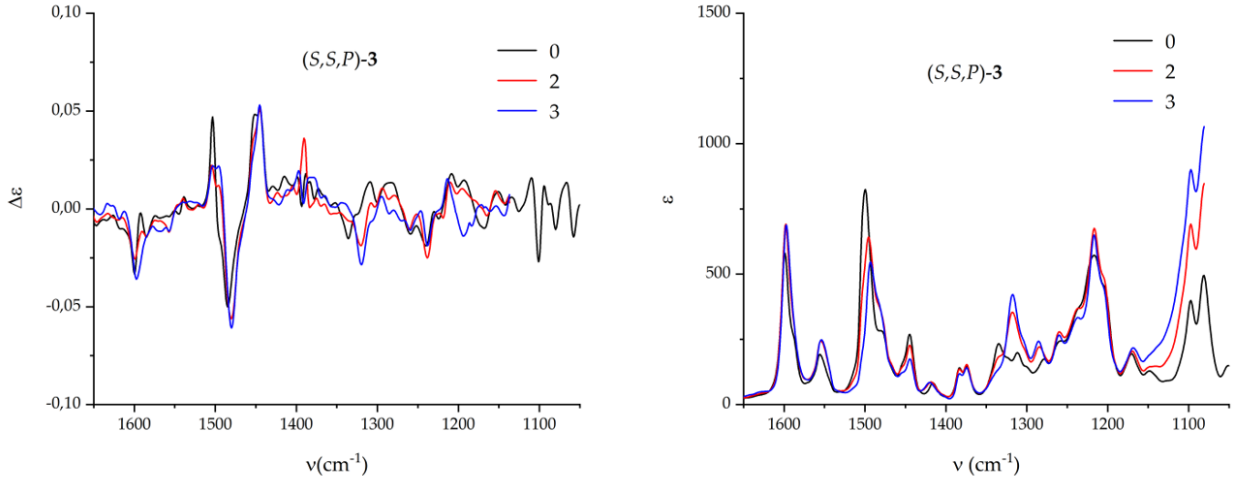


Figure S141. VCD (left) and IR (right) spectra for the compound (*S*,*S*,*P*)-**3** in CH_2Cl_2 solution and after addition of $AgBF_4$ salt (salt: compound molarity ratios are indicated by labels).

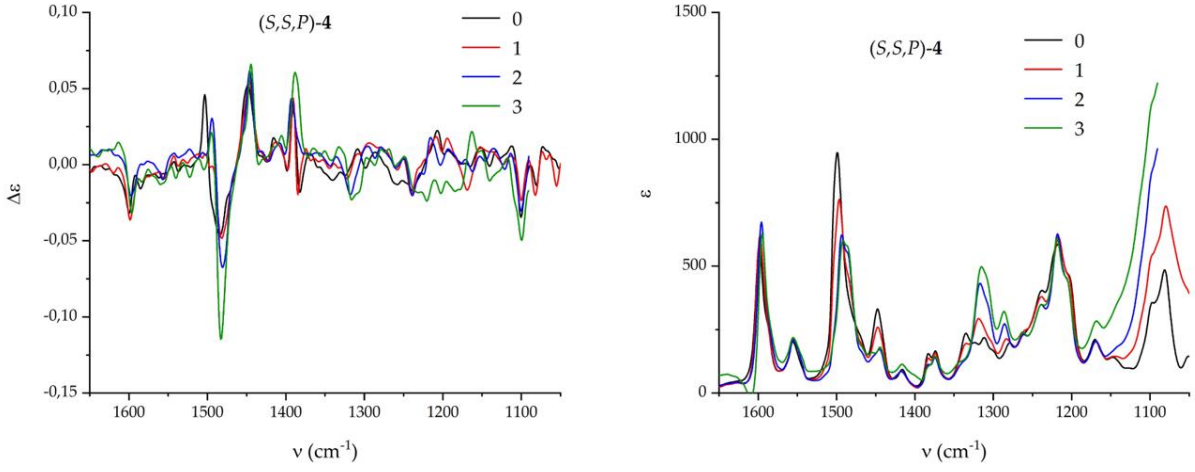


Figure S142. VCD (left) and IR (right) spectra for the compound (*S,S,P*)-**4** in CH_2Cl_2 solution and after addition of $AgBF_4$ salt (salt: compound molarity ratios are indicated by labels).

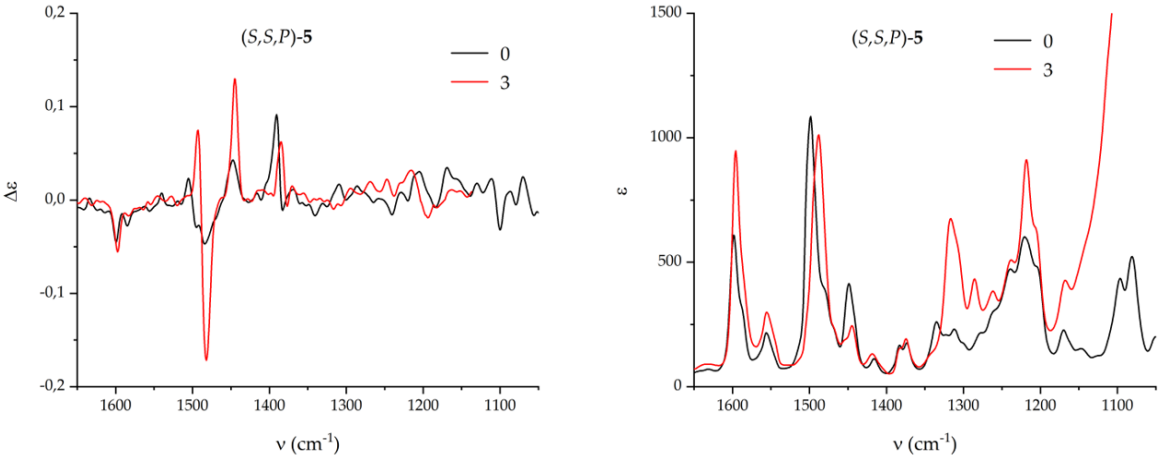


Figure S143. VCD (left) and IR (right) spectra for the compound (*S,S,P*)-**5** in CH_2Cl_2 solution and after addition of $AgBF_4$ salt (salt: compound molarity ratios are indicated by labels).

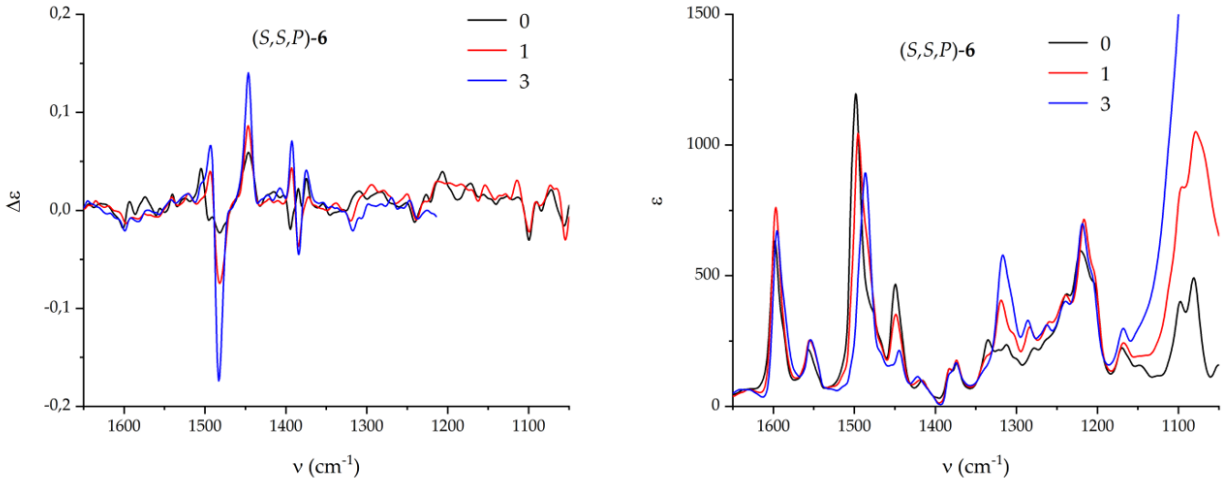


Figure S144. VCD (left) and IR (right) spectra for the compound (*S,S,P*)-**6** in CH_2Cl_2 solution and after addition of $AgBF_4$ salt (salt: compound molarity ratios are indicated by labels).

7. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) TRACES

HPLC analysis were performed on an JASCO LC-4000 Series equipped with the following modules: preparative pump (up to 30 mL/min, PU-4087), preparative autosampler (AS4058), preparative column oven (CO4065), PDA detector (MD4010, 1024 element photometric diode array with measurement wavelength range from 190nm to 900nm and resolution of 1nm) and automatic sample fraction collector advantec (CHF122SC). The column temperature was set at 20 °C and the mobile phase used was Hexane:AcOEt (8:2). The wavelength selected for the peak detection was 280 nm and the flow was constant during the operation: 30 mL/min.

All the samples were purificated with these methodologies, isolating and characterizing the main peak.

Table S9. Isolated peaks

COMPOUND	Acquisition Time (min)
(*S*,*S*,*P*)-**2**	19.63
(*S*,*S*,*P*)-**3**	24.66
(*S*,*S*,*P*)-**4**	53.33
(*S*,*S*,*P*)-**5**	13.92
(*S*,*S*,*P*)-**6**	22.62

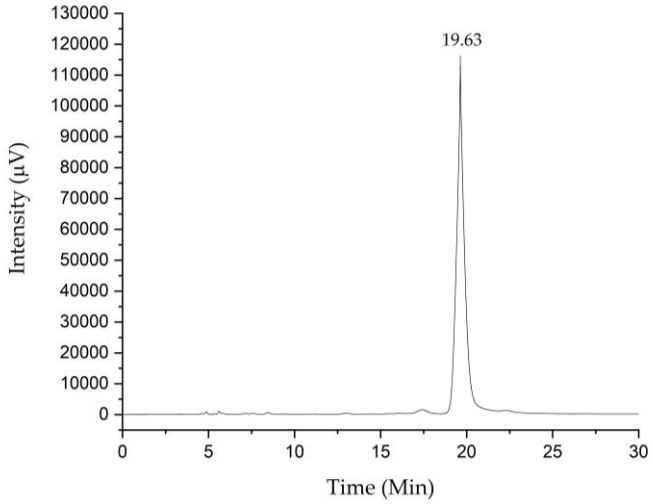


Figure S145. Example of HPLC chromatogram of (*S*,*S*,*P*)-**2**

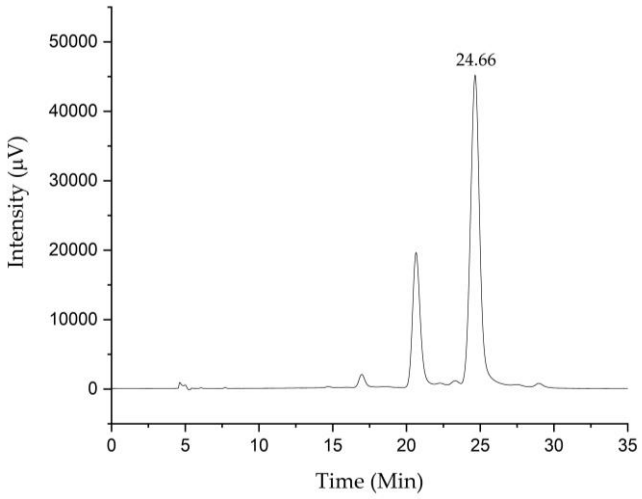


Figure S146. HPLC chromatogram of (*S*,*S*,*P*)-**3**

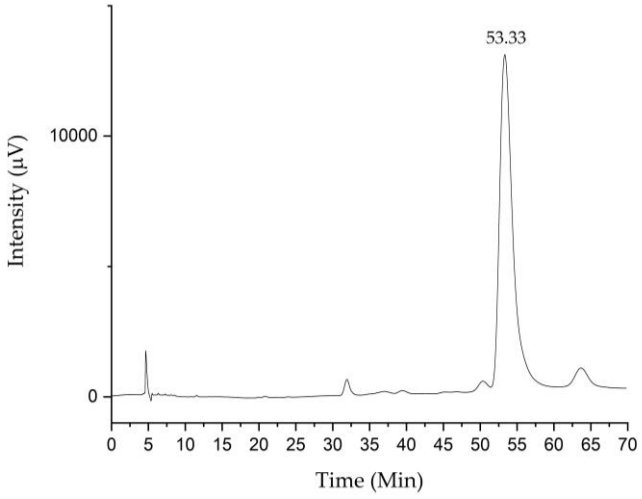


Figure S147. HPLC chromatogram of (*S,S,P*)-**4**

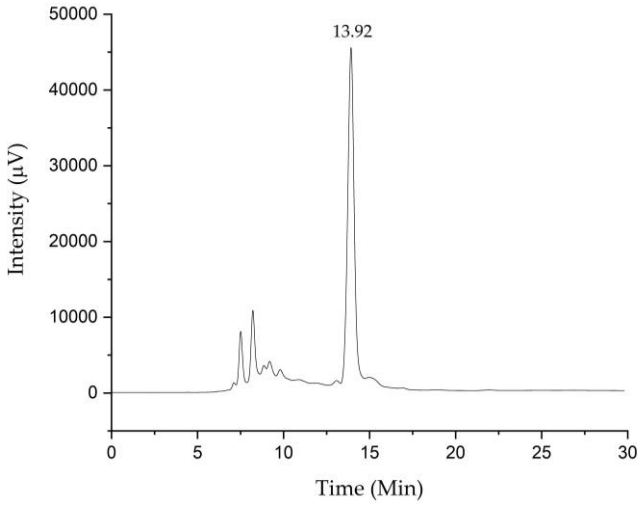


Figure S148. HPLC chromatogram of (*S,S,P*)-**5**

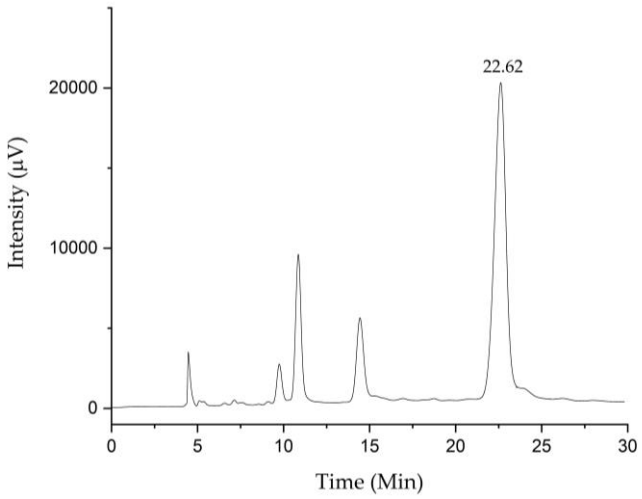


Figure S149. HPLC chromatogram of (*S,S,P*)-**6**

8. DFT calculations

Structures have been optimized at the B3LYP/6-31G** level with Gaussian 16,[12a] and IR, VCD spectra have also been calculated with this basis set.[13] The Stuttgart/Cologne energy-consistent pseudopotentials ECP28MDF_VDZ has been used for silver.[14]

Spectra have been simulated as superposition of Lorentzian functions, linewidth 12 cm^{-1} for all transitions. To facilitate comparison of observed and calculated spectra, 0.98 scaling factor was applied to the calculated wavenumbers.

In Ag-containing complexes, 6-31G* was used for all atoms but Ag for which LANL2DZ basis set (valence and ECP) were used (PCM dichloromethane). These calculations were performed using Gaussian 09.[12b]

On the other hand, in order to check that the basis set does not substantially vary the geometry nor the conformer populations, compounds were also optimized using M06/6-31g*, confirming that in both cases the most populated conformer was the helicoidally twisted one. However, we observed slight differences in the geometry, and we obtained more stacked structures when using M06 functional. In addition, ECD calculations performed with M06 provided high rotational strengths for the first transition, the calculated values agreeing with the experimental ones. That is the reason why we chose M06 to discuss ECD response.

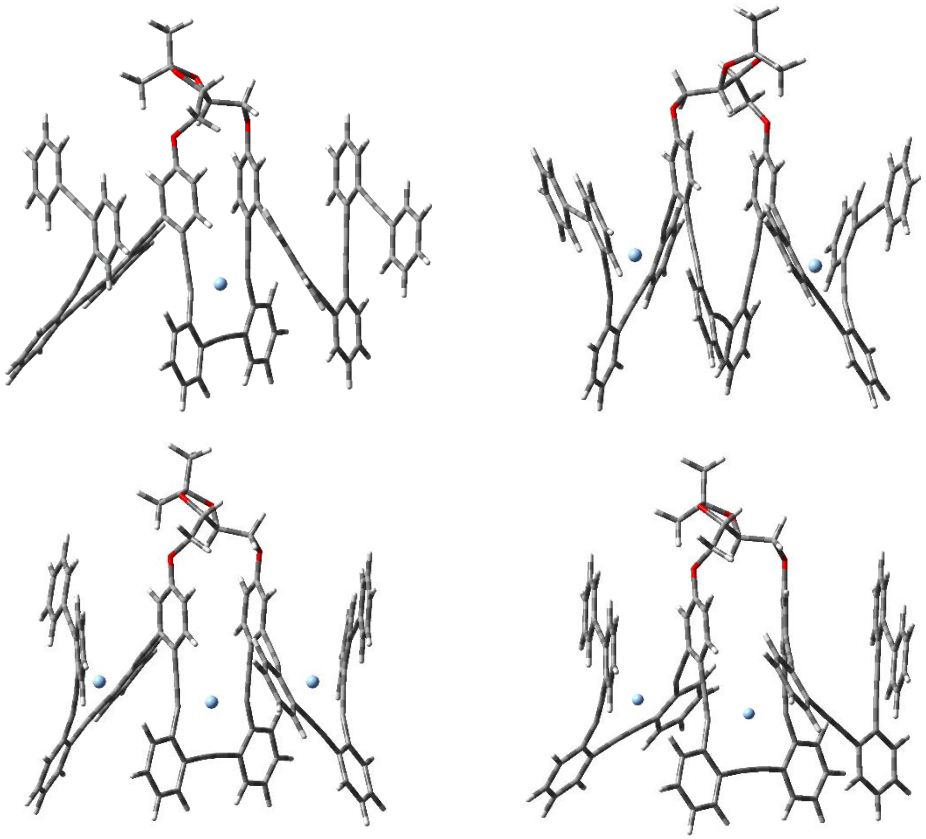


Fig. S150. Optimized structure for compound (*S,S,P*)-**5** with one Ag cation (top left), two Ag cations either symmetrically (top right) or non-symmetrically disposed (bottom right) and three cations (bottom left).

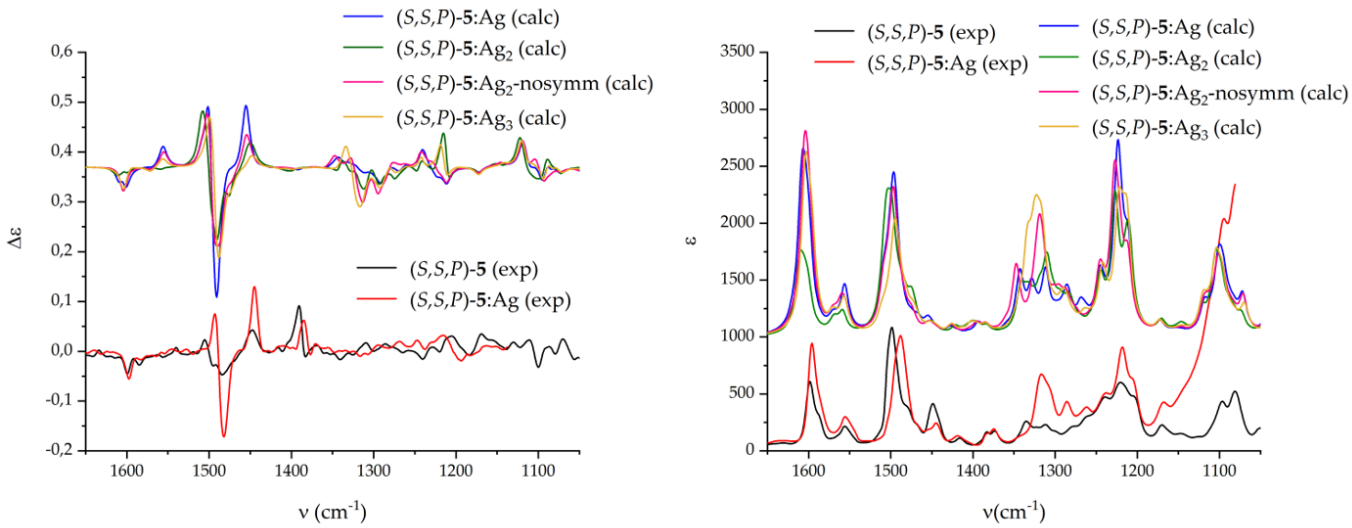


Fig. S151. Comparison of calculated and experimental spectra of compound (*S,S,P*)-**5**. Calculations have been done for helicoidal structures of Figure S144, with one, two (symmetrically and non-symmetrically disposed) and three silver cations.

Compound (*S,S,P*)-**5** revealed to be quite efficient in incorporating silver ions and has sufficient length to show an enhancement of VCD signals when it is guided to form a regular helix by the presence of silver. The (+,-,+) triplet at about 1450-1500 cm^{-1} show similar intensity in short and long chains (from (*S,S,P*)-**2** to (*S,S,P*)-**6**), suggesting that the central portion of the backbone rigidified by the staple is the one responsible for this signal in all compounds in CD_2Cl_2 solution. Only in presence of silver, the longer backbone assumes an ordered structure able to show an intensification of the triplet.

Conformational search for compound (S,S,P)-1

After MM conformational search, all structures within 5 Kcal/mol have been considered presenting both helicity and have been optimized at B3LYP/6-31g** level, with dichloromethane treated with PCM model. Only three conformers have been obtained with non-negligible populations (Table S10): they all present *P* helicity but different relative spatial orientations of the bromine atoms (*out-out, out-in and in-in*), and considering calculated energy they are nearly equally populated. They present similar CD and absorption spectra as calculated at M06/6-31g** level (Figure S152). It is noticeable the high g_{abs} value of the first electronic transition, particularly considering conformer *in/in* (table S10).

Table S10. Calculated energies and population factors of the three principal conformers of compound (*S,S,P*)-**1.** Calculated energy, wavelength, dipole and rotational strengths, angle between electric dipole transition moment and magnetic dipole transition moment and dissymmetry ratio as obtained by TD-DFT calculations for the first electronic transition.

conf.	Kcal/mol	Pop (%)	eV	nm	D	R	E-M	g
in/in	0.09	32.1	3.17	391	96168	389	73	0.0162
in/out	0.12	30.5	3.18	389	112481	225	81	0.0080
out/out	0.00	37.4	3.17	391	126760	203	82	0.0064

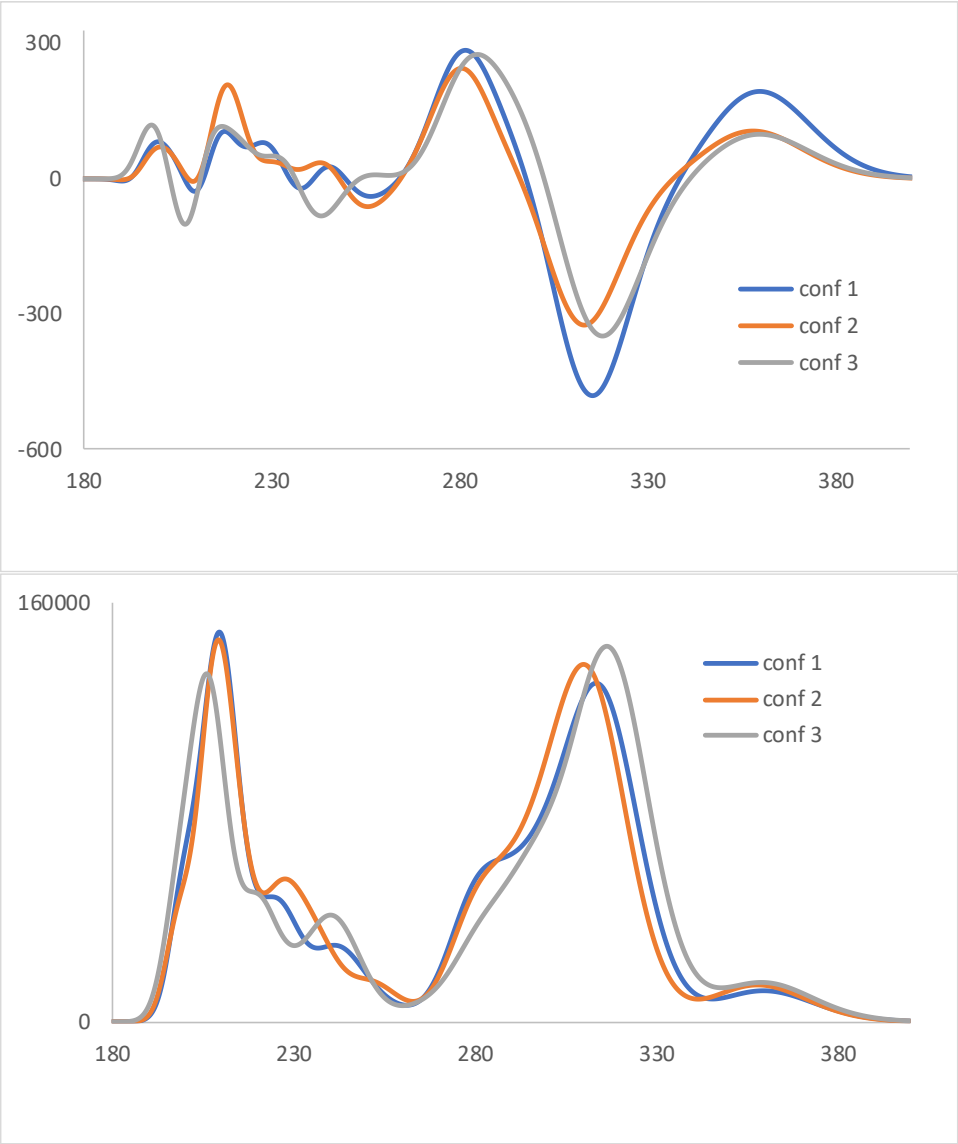


Figure S152. Calculated CD and absorption spectra of the three principal conformers of compound (*S,S,P*)-**1**. Calculated spectra are 20 nm shifted

Conformational search for compound (S,S,P)-2

A systematic conformational search has been conducted for (*S,S,P*)-**2** compound as reported below.

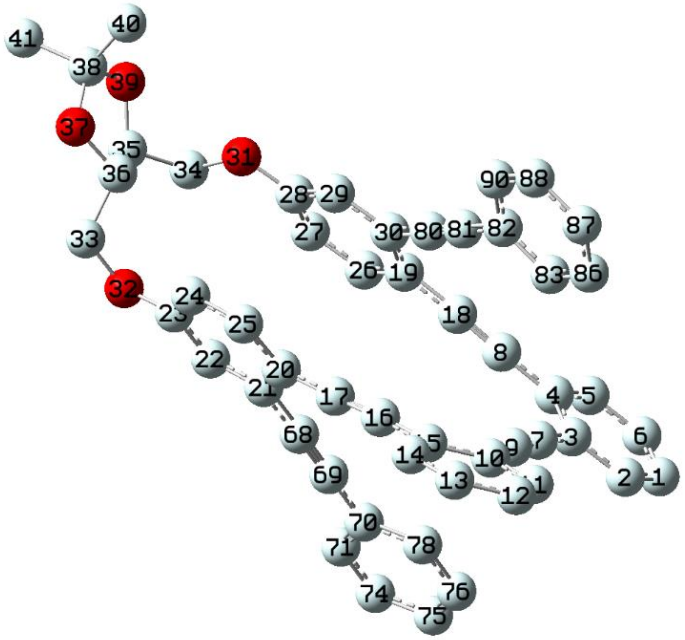


Table S11. Data of the main conformers of (*S,S,P*)-**2**: significant dihedral angles of the backbone (relative to "helicity") and of the staple are reported. A classification of the calculated CD spectrum as (+,-,+) indicated as I or (-,+,-) indicated as II is also given

conf.	Kcal /mol	**pop(%)**	21-20-15-10	15-10-3-4	3-4-19-30	Conf. type	28,31,34,35	31,34,35,36	34,35,36,33	32,33,36,35	23,32,33,36
1	0.00	*76.5%*	42	23	45	I	151	-50	-88	65	80
2	1.59	*5.2%*	151	-24	147	II	78	62	-147	74	-98
3	1.72	*4.2%*	41	33	172	I-a	-75	178	-91	-53	128
4	1.80	*3.6%*	138	-15	145	II	128	-57	-101	50	86
5	2.10	*2.2%*	138	-16	-44	III	132	-55	-101	49	86
6	2.12	*2.1%*	152	-24	-37	III	-149	95	-79	88	-160
7	2.24	*1.8%*	155	-28	150	II	151	-48	-86	103	-92
8	2.45	*1.2%*	156	-29	139	II	-141	159	-94	68	-107
9	2.58	*1.0%*	43	29	-173	I-a	-75	177	-94	76	-122
10	2.73	*0.8%*	165	-29	-45	III	-127	155	-93	71	-138
11	2.92	*0.6%*	137	-28	-35	III	-104	70	-93	160	-144
12	3.03	*0.5%*	158	-29	-42	III	-139	161	-94	69	-109
13	3.86	*0.1%*	35	23	-152	I-a	-121	73	-95	179	-76
14	3.94	*0.1%*	44	22	37	I	-81	176	-94	74	-127
15	5.71	*0.0%*	153	-30	153	II	122	-30	-74	-30	123
1,4-Ag	0.00	*95.9%*	57	6	65		147	-52	-91	63	83
3-Ag	2.19	*2.4%*	72	3	-151		-80	168	-96	-51	131
2-Ag	2.37	*1.7%*	105	-1	99		78	73	-146	84	-104

One conformer is by far the most populated one and the OPE backbone describes a well-defined *P* helix. Considering higher energy conformers, a variety of structures is possible in principle: I, P helix; I-a, partially P folded (two positive dihedral angles); II, unfolded; III, partially M folded.

Below, the four lowest energy conformers are shown. Starting from these structures an Ag ion has been added and the complex optimized giving three different structures, the only populated one is the first one. As expected, silver ion seems to induce and stabilize an ordered helical *P* structure.

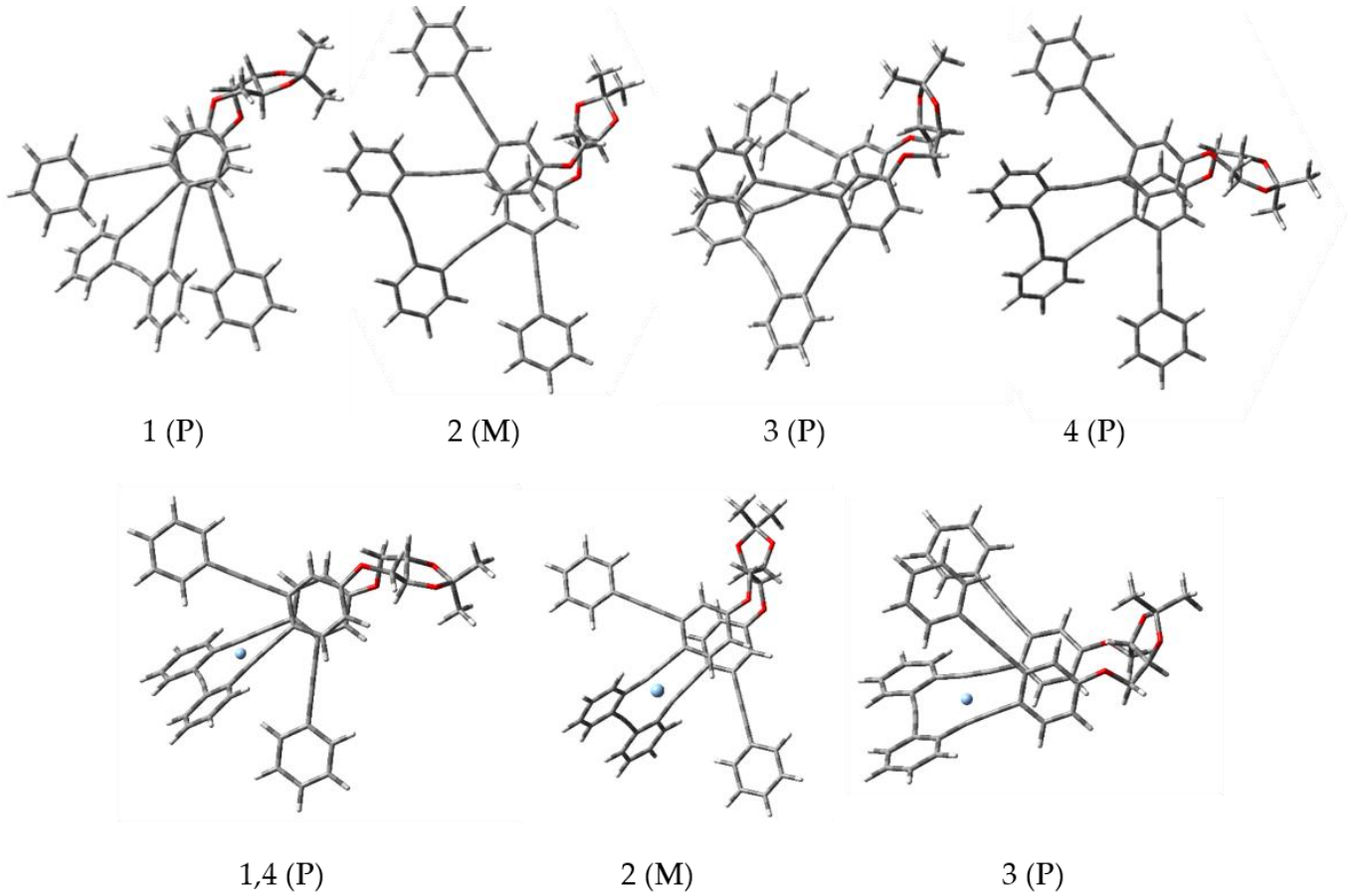


Figure S153. Lower energy conformers of compound (*S*,*S*,*P*)-**2**.

To elucidate how the conformer classification is reflected in the calculated spectra we report both VCD and ECD spectra for all conformers below.

Figure S154. Calculated ECD (left) and VCD (right) spectra for all optimized conformers of the compound (*S,S,P*)-**2** (see conformational analysis of Table S7).

Depending on backbone dihedral angles, calculated ECD spectra show (+,-,+) bands for conformers I (blue) and I-a (dark blue), which are P helix at least partially and in the case of extended conformers II (green). In case of two negative dihedral angles, conformers III, the CD spectra invert and give low CD. VCD spectra at about 1500 cm^{-1} correlate with ECD pattern: conformers I (blue) and I-a (dark blue), P helix, give the observed triplet (+,-,+), conformers III (yellow) with two negative dihedral angles, partially M, show the opposite triplet (-,+,-), finally extended conformers II (green) are somehow intermediate (-,+,-,+).

Excited state structure of compound (S,S,P)-2.

Starting from the lowest energy ground state structure, optimization has been performed in the first excited state: the helix are nearly superimposable in the two ground and excited state however differences can be found in the bond length alteration (BLA) of the C-C≡C-C groups as described in the following table.

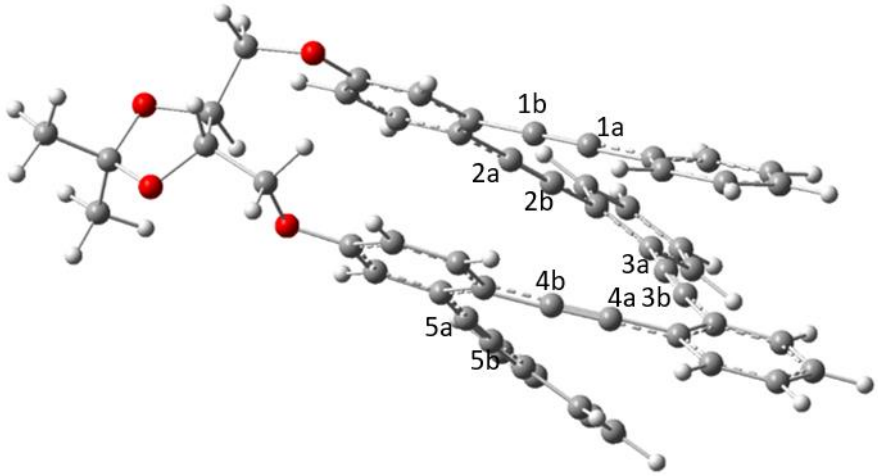
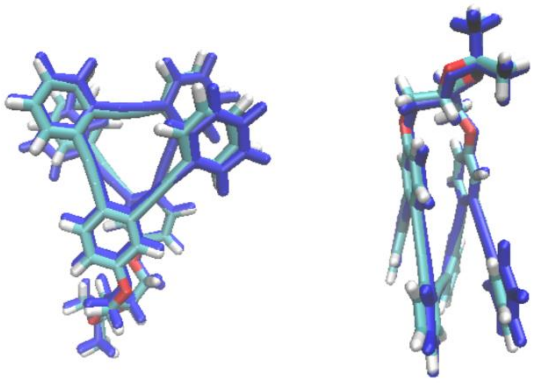


Table S12. Bond length alteration of the C–C≡C–C



*	*	BLA-ground	BLA-excited
1	a	0.208	0.200
1	b	0.206	0.193
2	a	0.204	0.168
2	b	0.205	0.162
3	a	0.207	0.149
3	b	0.207	0.148
4	a	0.206	0.162
4	b	0.205	0.167
5	a	0.206	0.192
5	b	0.208	0.199

*C-C≡ is indicated in the figure above by a number (referring to the C-C≡ C-C segment) and a letter (a first single bond length minus triple bond length, b second bond length minus triple bond length.

One may notice that the difference in bond length between single and triple bonds is less pronounced in the excited state and the major changes in BLA values are found in the inner part of the helix (segment 3 of the helix).

Compound (S,S,P)-2: characteristics of the first absorption transition and emissive transition

Calculated at M06/6-31g** level.

	eV	*nm*	*D*	*R*	*g*
0→1	3.0	411	41568	645	0.062
0←1	2.3	533	52040	616	0.047

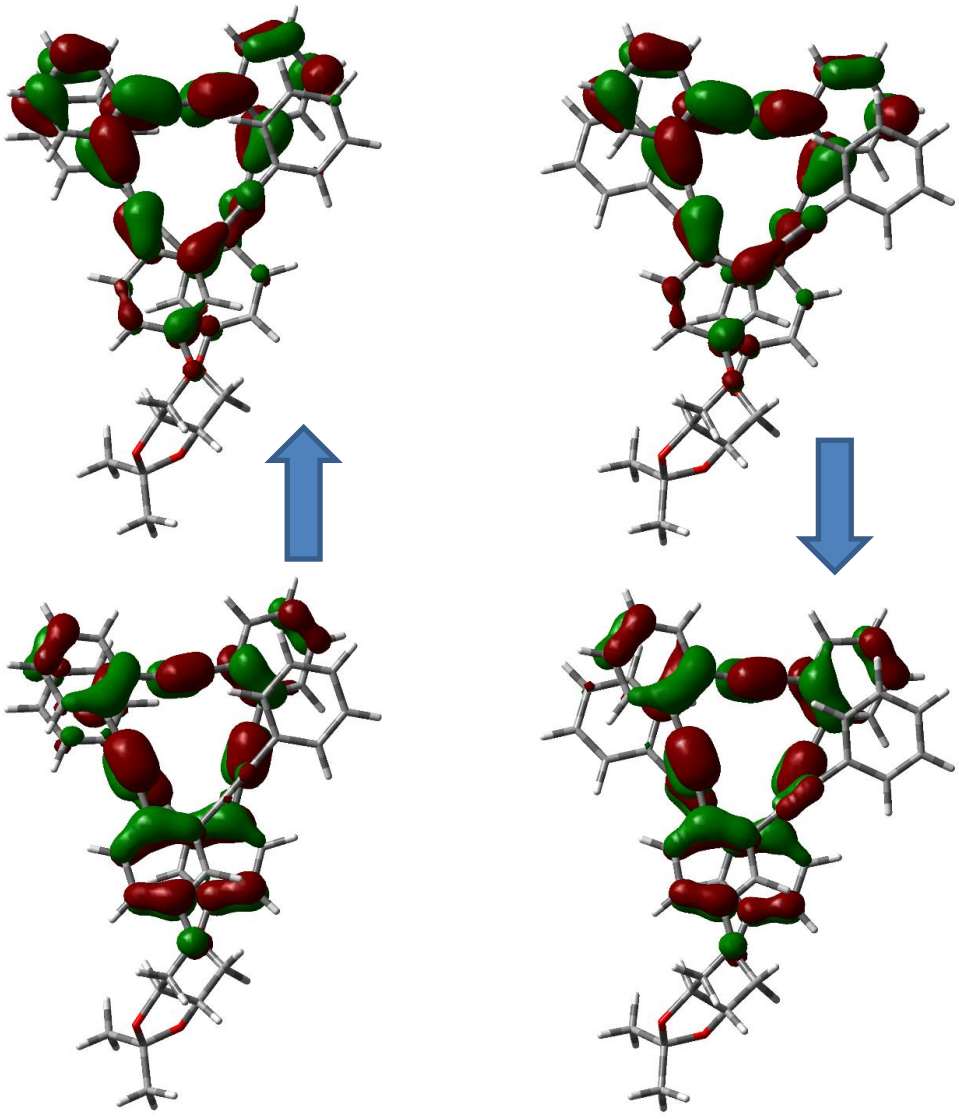
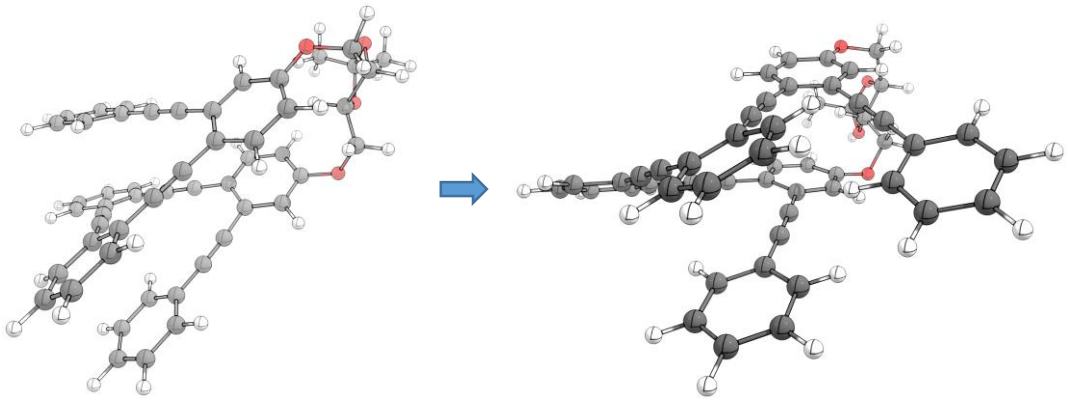


Figure S155. HOMO and LUMO orbitals involved in the first absorption feature and in emission.

Compound (S,S,P)-2: study of the rotational barrier of the unfoldedconformer



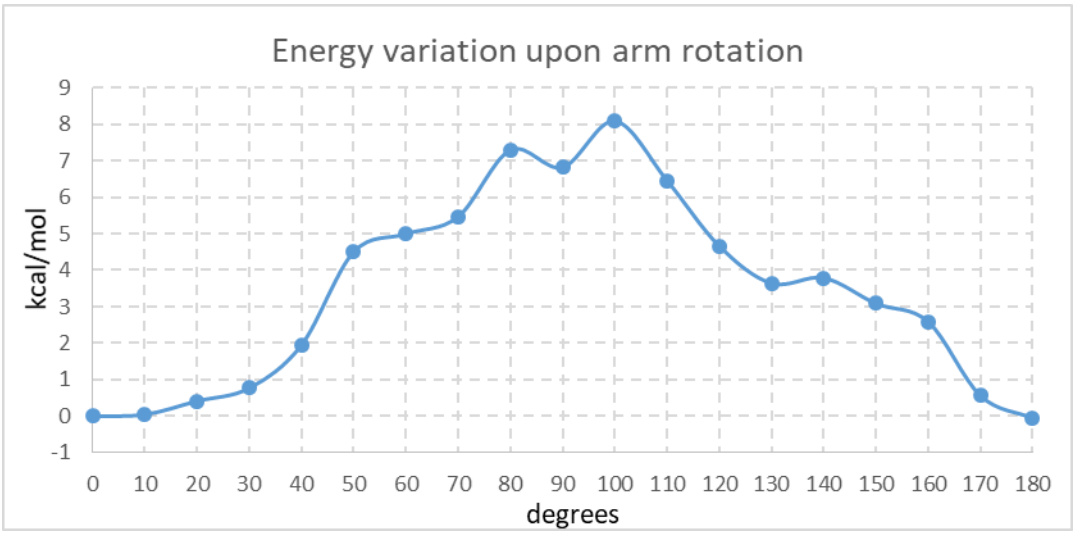


Figure S156. Up: structures of semi-folded and unfolded compound (*S,S,P*)-**2**. Down: energetic profile obtained after the rotation of one arm in 10º steps from the folded to the unfolded structure.

Representation of the magnetic dipole transition moments of compounds (S,S,P)-2 to (S,S,P)-6 in absence and presence of Ag(I)

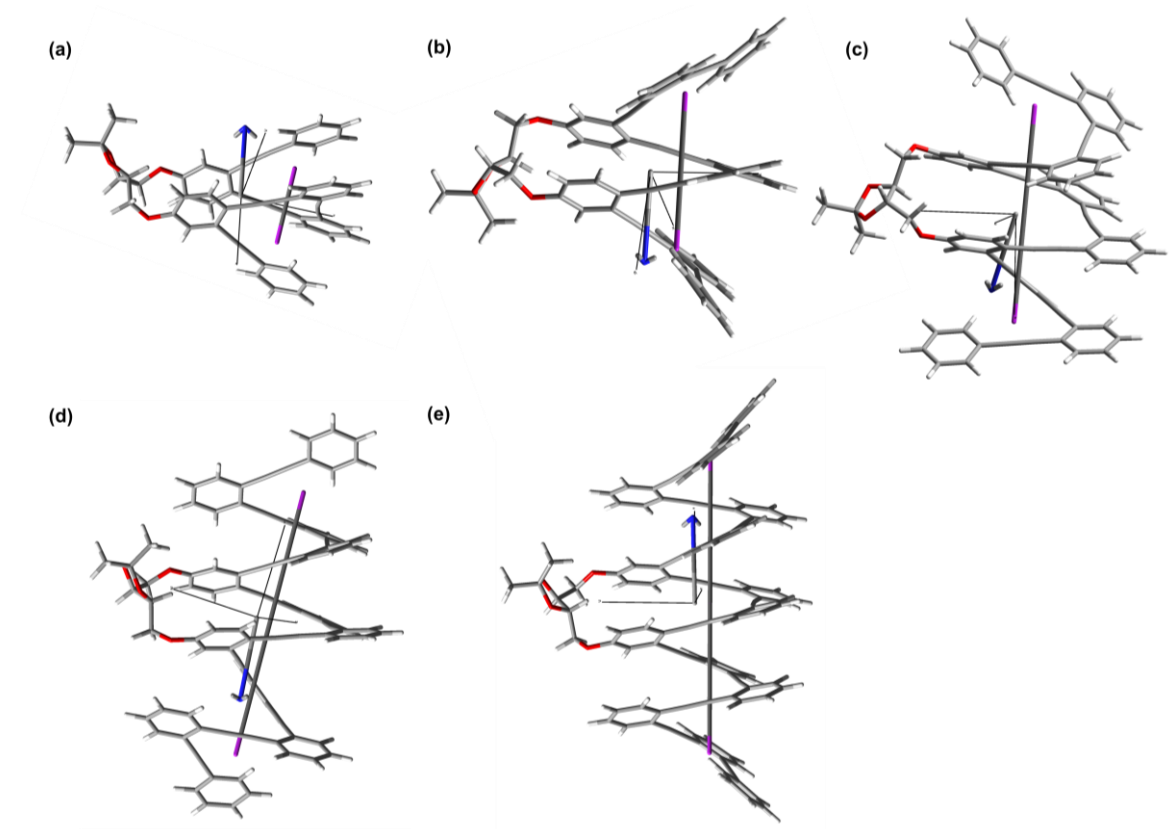


Figure S157. Calculated structures, helix axis and magnetic dipole transition moments of (a) (*S*,*S*,*P*)-**2**, b) (*S*,*S*,*P*)-**3**, c) (*S*,*S*,*P*)-**4**, d) (*S*,*S*,*P*)-**5**, e) (*S*,*S*,*P*)-**6**.

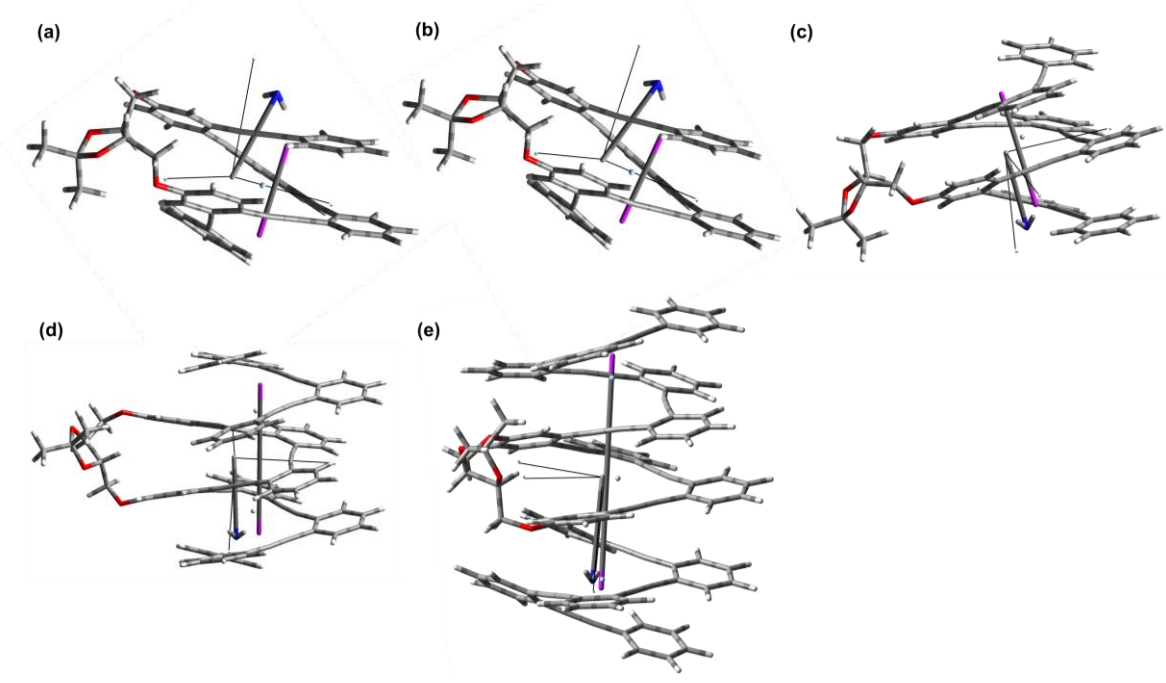


Figure S158. Calculated structures, helix axis and magnetic dipole transition moments of (a) (*S*,*S*,*P*)-**2:Ag**, b) (*S*,*S*,*P*)-**3:Ag**, c) (*S*,*S*,*P*)-**4:Ag**$_2$, d) (*S*,*S*,*P*)-**5:Ag**$_2$, e) (*S*,*S*,*P*)-**6:Ag**$_3$.

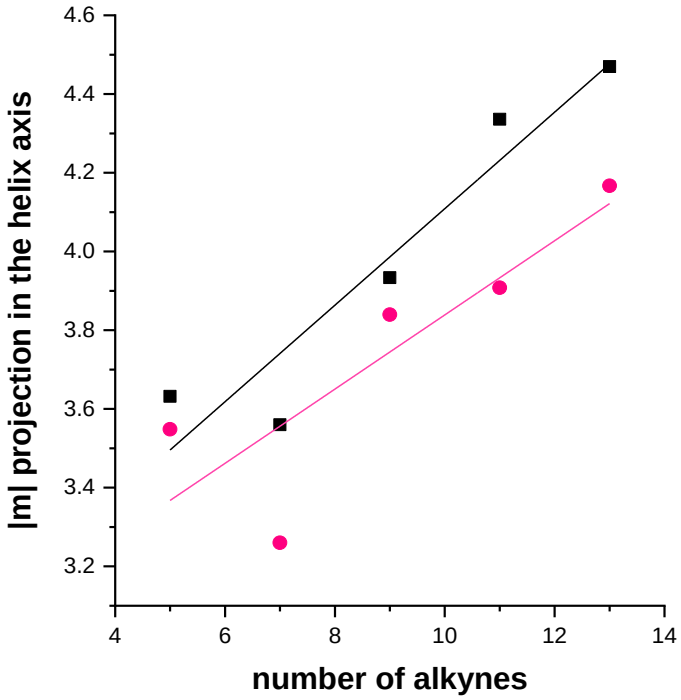


Figure S159. a) Linear fitting of |m| projection in the helix axis with the number of alkynes of compounds (*S*,*S*,*P*)-**2-6** in CH_2Cl_2 solutions in absence of Ag(I) (black squares, y = 2.88+ 0.12x, R^2 = 0.90) and silver complexes (*S*,*S*,*P*)-**2**:Ag, (*S*,*S*,*P*)-**3**:Ag, (*S*,*S*,*P*)-**4**:Ag_2, (*S*,*S*,*P*)-**5**:Ag_2 and (*S*,*S*,*P*)-**6**:Ag_3 (pink circles, y = 2.89+0.09x, R^2 = 0.73).

Coordinates of optimized structures for compounds (*S*,*S*,*P*)-1 to (*S*,*S*,*P*)-6 and for complexes (*S*,*S*,*P*)-1:Ag, (*S*,*S*,*P*)-2:Ag, (*S*,*S*,*P*)-3:Ag, (*S*,*S*,*P*)-4:Ag_2, (*S*,*S*,*P*)-5:Ag_2, (*S*,*S*,*P*)6:Ag_3.

Table S13. Atomic coordinates for the DFT optimized structure of (*S*,*S*,*P*)-**1**

(	X	Y	Z
C	-7.22465	0.32484	-1.04054
C	-6.99984	0.9495	-2.41291
H	-7.50253	1.91826	-2.4761
H	-5.93036	1.08958	-2.58858
H	-7.3989	0.29747	-3.19482
C	-8.69704	0.14275	-0.69031
H	-9.19355	-0.46845	-1.44856
H	-9.19796	1.11363	-0.64228
H	-8.79328	-0.34871	0.28118
O	-6.6206	1.13468	-0.01403
O	-6.53753	-0.93651	-1.00694
C	-5.41645	0.49789	0.40548
H	-4.57603	0.79539	-0.23378
C	-5.73269	-0.98511	0.16846
H	-6.31153	-1.38536	1.01708
C	-5.15031	0.90404	1.85333
H	-5.12596	1.99402	1.94844
H	-5.94336	0.52627	2.50237
C	-4.54444	-1.9082	-0.03697
H	-4.89041	-2.89429	-0.36769
H	-4.02894	-2.01757	0.92221
O	-3.94381	0.30911	2.34839
C	-2.72812	0.81739	1.98765
C	-0.10071	1.63293	1.31141
C	-2.52505	2.00702	1.27587
C	-1.62388	0.05059	2.38881
C	-0.34261	0.45514	2.05047
C	-1.23001	2.39612	0.95233
H	-3.35466	2.62651	0.9598
H	-1.78976	-0.86126	2.94891
H	-1.07591	3.31077	0.39024
Br	1.12469	-0.63362	2.59054
C	1.19409	2.06074	0.90932
C	2.2531	2.50248	0.50338
C	3.4374	3.14169	0.03946
C	5.72342	4.53011	-0.85273
C	4.62454	2.42594	-0.2848
C	3.429	4.54466	-0.10306
C	4.55381	5.23222	-0.54361
C	5.75473	3.14656	-0.72343
H	2.52067	5.08393	0.14378
H	4.5204	6.31251	-0.64323
H	6.65679	2.59497	-0.96595
H	6.60683	5.05961	-1.19512
C	4.72881	1.00803	-0.18958
C	4.96528	-0.1864	-0.1651
C	5.35965	-1.55442	-0.11145
C	6.24122	-4.22702	0.02702
C	4.4327	-2.62243	-0.28209
C	6.7162	-1.86075	0.11641
C	7.1537	-3.17899	0.1858
C	4.89829	-3.94946	-0.20487
H	7.41856	-1.04372	0.24314
H	8.20332	-3.38936	0.36491
H	4.18641	-4.75784	-0.33398
H	6.57685	-5.25779	0.08135
C	3.05239	-2.37634	-0.52145
C	1.86633	-2.19373	-0.72039
C	0.46281	-2.01987	-0.85809
C	-2.33845	-1.64316	-0.95454
C	-0.42334	-2.90541	-0.21385
C	-0.11603	-0.96239	-1.59202
C	-1.48686	-0.77127	-1.64868
C	-1.80204	-2.7339	-0.25663
H	-0.00661	-3.7371	0.34357
H	-1.9128	0.06053	-2.1959
H	-2.44298	-3.44106	0.25501
Br	1.01039	0.27206	-2.51123
O	-3.66455	-1.34193	-1.01496

Low frequencies --- 14.5584 15.1193 22.685
-6869.784056
Zero-point correction= 0.526977 (Hartree/Particle)
Thermal correction to Energy= 0.564592

Thermal	correction	to	Enthalpy=	0.565536	
Thermal	correction	to	Gibbs Free	Energy=	0.453658
Sum of	electronic	and	zero-point	Energies=	-6869.257079
Sum of	electronic	and	thermal	Energies=	-6869.219465
Sum of	electronic	and	thermal	Enthalpies=	-6869.21852
Sum of	electronic	and	thermal	Free Energies=	-6869.330399

Table S14. Atomic coordinates for the DFT optimized structure of (*S*,*S*,*P*)-**2**

	X	Y	Z
C	6.52715	-2.61599	-1.49723
C	6.02771	-1.49675	-0.84906
C	4.65163	-1.22369	-0.83293
C	3.76982	-2.10531	-1.50276
C	4.29324	-3.23617	-2.14498
C	5.65612	-3.49137	-2.14426
C	4.19807	-0.06535	-0.14118
C	2.37226	-1.85816	-1.53612
C	3.93887	0.9553	0.46798
C	3.82643	2.20517	1.13909
C	4.96452	3.02546	1.18533
C	4.93684	4.25826	1.81718
C	3.76004	4.70241	2.41773
C	2.62421	3.90958	2.38041
C	2.63275	2.65618	1.74857
C	1.43138	1.8963	1.74182
C	0.34626	1.35257	1.80623
C	1.17457	-1.66058	-1.58238
C	-0.22468	-1.42745	-1.59492
C	-0.94645	0.76875	1.8754
C	-1.13004	-0.63744	1.84863
C	-2.42016	-1.16357	1.9174
C	-3.53051	-0.32709	2.02337
C	-3.35829	1.05897	2.05118
C	-2.07687	1.58597	1.97858
C	-1.12647	-2.49315	-1.53046
C	-2.49658	-2.28242	-1.47884
C	-2.98842	-0.97384	-1.47883
C	-2.11115	0.10501	-1.56795
C	-0.73477	-0.10336	-1.62875
O	-4.30427	-0.66076	-1.39878
O	-4.73104	-0.96246	2.1115
C	-5.93036	-0.20985	2.01317
C	-5.19892	-1.65395	-0.92798
C	-6.42807	-0.98321	-0.37437
C	-6.18506	0.18038	0.57496
O	-7.4093	0.87693	0.49309
C	-7.87943	0.74107	-0.84751
O	-7.17381	-0.36857	-1.40453
C	-7.53409	1.96895	-1.65928
C	-9.35955	0.44828	-0.79174
H	7.5969	-2.80795	-1.49678
H	6.69808	-0.81182	-0.33527
H	3.60509	-3.91011	-2.64953
H	6.04126	-4.37212	-2.65137
H	5.8739	2.67148	0.70524
H	5.83168	4.87474	1.83917
H	3.72882	5.66774	2.91628
H	1.70103	4.24636	2.84575
H	-2.57212	-2.24016	1.89496
H	-4.20434	1.73453	2.12906
H	-1.94031	2.66426	1.99952
H	-0.7344	-3.50746	-1.50677
H	-3.16895	-3.13368	-1.43485
H	-2.51591	1.11407	-1.56521
H	-6.72934	-0.87128	2.36635
H	-5.91524	0.67107	2.6683
H	-4.73419	-2.23537	-0.11842
H	-5.47705	-2.34198	-1.73931
H	-7.03189	-1.75578	0.14138
H	-5.35211	0.79252	0.1888
H	-7.83721	1.82889	-2.70192
H	-8.04855	2.84795	-1.25809
H	-6.45248	2.13969	-1.63295
H	-9.76002	0.33038	-1.80344
H	-9.53148	-0.47466	-0.22827
H	-9.89023	1.26864	-0.29761
C	-0.00492	-1.49935	1.75711
C	0.9805	-2.20575	1.6911
C	2.13907	-3.0279	1.6259
C	2.05942	-4.33757	1.12862
H	1.09818	-4.71534	0.78637
H	3.12923	-6.14264	0.67982
C	3.19685	-5.12941	1.06851
C	4.42273	-4.6289	1.50324
C	4.50912	-3.32957	1.99571
H	5.46723	-2.933	2.32369
C	3.37666	-2.52954	2.05777
H	3.4338	-1.50718	2.42488

C	0.16949	0.98842	-1.71186
C	1.00213	1.86897	-1.78506
C	2.02766	2.852	-1.85335
C	3.2792	2.50928	-2.3882
H	3.43396	1.49678	-2.75593
H	5.2697	3.17262	-2.83789
C	4.30158	3.44633	-2.42536
C	4.09143	4.73028	-1.92762
C	2.85135	5.07857	-1.39753
H	2.6896	6.07825	-1.00128
C	1.82235	4.14828	-1.35993
H	0.85523	4.40521	-0.93298
H	4.89672	5.46072	-1.95021
H	5.31313	-5.25085	1.45102

Low frequencies --- 9.8973 12.0426 15.1037
-2342.019811
Zero-point correction= 0.72811 (Hartree/Particle)
Thermal correction to Energy= 0.77666
Thermal correction to Enthalpy= 0.777604
Thermal correction to Gibbs Free Energy= 0.638549
Sum of electronic and zero-point Energies= -2341.2917
Sum of electronic and thermal Energies= -2341.243151
Sum of electronic and thermal Enthalpies= -2341.242207
Sum of electronic and thermal Free Energies= -2341.381262

Table S15. Atomic coordinates for the DFT optimized structure of (*S,S,P*)-**3**

	X	Y	Z
C	-4.54719	1.78771	4.15939
C	-4.49487	1.17934	2.91141
C	-3.31336	1.18254	2.1399
C	-2.16059	1.83603	2.65762
C	-2.2369	2.44232	3.92972
C	-3.41052	2.4208	4.67288
C	-3.35172	0.52599	0.87567
C	-0.92039	1.91545	1.96107
C	-3.56421	-0.08245	-0.1578
C	-3.97626	-0.7388	-1.35357
C	-5.32848	-0.63478	-1.7391
C	-5.79759	-1.24694	-2.89573
C	-4.92156	-1.98328	-3.69993
C	-3.58491	-2.10467	-3.33771
C	-3.088	-1.49679	-2.16748
C	-1.71282	-1.65224	-1.8384
C	-0.52723	-1.81759	-1.61684
C	0.19454	2.07574	1.49621
C	1.55076	2.24763	1.09978
C	0.87941	-1.92884	-1.44201
C	1.4764	-1.99399	-0.14904
C	2.87326	-1.99299	-0.03655
C	3.68661	-1.94021	-1.17221
C	3.10658	-1.94298	-2.44874
C	1.72111	-1.93121	-2.56785
C	2.53337	2.40928	2.09834
C	3.87598	2.54686	1.7804
C	4.2826	2.52804	0.43901
C	3.33028	2.3933	-0.57256
C	1.96377	2.25962	-0.26164
O	5.6212	2.71798	0.19683
O	5.03198	-1.9025	-0.94354
C	5.8912	-1.33643	-1.93968
C	6.26528	1.87839	-0.77141
C	6.50944	0.48135	-0.22299
C	7.00066	-0.54213	-1.26259
O	7.86619	-1.39496	-0.51949
C	8.13557	-0.80701	0.77042
O	7.57673	0.50685	0.72185
C	9.63928	-0.67435	0.96304
C	7.46152	-1.65571	1.84782
H	-5.46964	1.7671	4.73102
H	-5.37085	0.68198	2.50906

H	-1.35279	2.93585	4.3192	C	-0.60279	2.09005	-3.40705
H	-3.44074	2.89766	5.6475	C	-0.26572	1.25352	-4.4878
H	-6.00197	-0.05861	-1.11363	H	0.64237	0.66367	-4.42359
H	-6.84308	-1.14949	-3.1707	H	-0.79901	0.52363	-6.43623
H	-5.28082	-2.46304	-4.60489	C	-1.07674	1.17721	-5.61537
H	-2.90066	-2.6776	-3.95448	C	-2.24553	1.94205	-5.68771
H	3.3379	-2.01652	0.94247	C	-2.59575	2.77984	-4.6343
H	3.71984	-1.95318	-3.34183	H	-3.49942	3.37774	-4.6868
H	1.27063	-1.91353	-3.55456	C	-1.79102	2.87314	-3.48224
H	2.22352	2.40928	3.13786	H	-2.88183	1.88603	-6.56529
H	4.62662	2.65953	2.55495	H	-2.65643	-2.38068	6.64492
H	3.62156	2.4156	-1.61577	C	-2.20806	-3.97013	2.35617
H	6.322	-2.13324	-2.55562	C	-2.56424	-4.72137	1.46748
H	5.32947	-0.65964	-2.59286	C	-2.96653	-5.59668	0.41677
H	7.21879	2.36307	-0.99225	C	-3.84477	-6.66952	0.67364
H	5.68378	1.8229	-1.69815	H	-4.21662	-6.82154	1.68173
H	5.58899	0.11255	0.2472	C	-4.22789	-7.52513	-0.3559
H	7.57278	-0.04083	-2.06001	H	-4.90384	-8.34866	-0.14617
H	9.85813	-0.19363	1.92043	C	-3.74573	-7.32723	-1.65277
H	10.10926	-1.66108	0.95402	C	-2.87694	-6.26467	-1.91705
H	10.06215	-0.06981	0.15727	H	-2.50235	-6.10655	-2.92399
H	7.62506	-1.2161	2.83566	C	-2.48712	-5.40268	-0.89525
H	6.38784	-1.72533	1.6586	C	-2.16448	3.75178	-2.428
H	7.8757	-2.66779	1.84242	C	-2.50378	4.52072	-1.54791
C	0.67797	-2.05575	1.02943	C	-2.8893	5.41887	-0.51048
C	0.02029	-2.13734	2.04948	C	-3.93708	6.34061	-0.71306
C	-0.71508	-2.20992	3.2672	H	-4.45097	6.35868	-1.66868
C	-1.80906	-3.11104	3.41759	C	-4.30631	7.21798	0.30307
H	-3.3231	-3.84171	4.7587	H	-5.11423	7.92394	0.13576
C	-2.49201	-3.15318	4.6484	C	-3.6421	7.19176	1.53262
C	-2.11465	-2.33194	5.70561	C	-2.60368	6.28018	1.74284
C	-1.04116	-1.4478	5.55713	H	-2.08789	6.25432	2.69799
H	-0.74437	-0.80503	6.37978	C	-2.22557	5.39858	0.73351
C	-0.3496	-1.39037	4.35141	H	-4.04617	-7.99684	-2.45298
H	0.48278	-0.70592	4.22797	H	-3.93308	7.87727	2.32278
C	1.02035	2.177	-1.32603	H	-1.81932	-4.57167	-1.09725
C	0.25577	2.15182	-2.27222	H	-1.42522	4.68419	0.89504

Low frequencies --- 7.1067 9.142 10.4944
-2956.452807
Zero-point correction= 0.908933 (Hartree/Particle)
Thermal correction to Energy= 0.9712
Thermal correction to Enthalpy= 0.972144
Thermal correction to Gibbs Free Energy= 0.800603
Sum of electronic and zero-point Energies= -2955.543873
Sum of electronic and thermal Energies= -2955.481606

Sum of electronic and thermal Enthalpies= -2955.480662
Sum of electronic and thermal Free Energies= -2955.652203

Table S16. Atomic coordinates for the DFT optimized structure of (*S,S,P*)-**4**

(*S,S,P*)-4	X	Y	Z
C	-1.31321	-5.17444	4.1036
C	-0.71615	-5.00648	2.86053
C	-0.82918	-3.79415	2.1464
C	-1.58321	-2.73157	2.71799
C	-2.17643	-2.92512	3.98396
C	-2.0461	-4.12608	4.66983
C	-0.17042	-3.71397	0.88502
C	-1.77825	-1.47056	2.08527
C	0.46464	-3.82541	-0.14862
C	1.17785	-4.13308	-1.3432
C	1.24128	-5.48203	-1.75012
C	1.91647	-5.85596	-2.90621
C	2.55063	-4.88469	-3.68798
C	2.50646	-3.54921	-3.30436
C	1.83122	-3.14699	-2.13454
C	1.8152	-1.7667	-1.78966
C	1.84567	-0.56963	-1.57319
C	-2.05285	-0.35175	1.68996
C	-2.36434	0.99547	1.35495
C	1.79433	0.84077	-1.40125
C	1.92109	1.45205	-0.11985
C	1.758	2.83878	0.00006
C	1.48561	3.63047	-1.11913
C	1.42483	3.04483	-2.39154
C	1.57186	1.6673	-2.51589
C	-2.57681	1.92551	2.393
C	-2.85536	3.2576	2.12782
C	-2.93247	3.70745	0.80214
C	-2.74843	2.80584	-0.24752
C	-2.47221	1.45013	0.01086
O	-3.2599	5.02896	0.62201
O	1.3061	4.96247	-0.8783
C	0.56189	5.74842	-1.81493
C	-2.57472	5.77565	-0.39144
C	-1.16917	6.15575	0.04849
C	-0.29145	6.76129	-1.06191
O	0.51932	7.7117	-0.37821
C	0.01658	7.90499	0.96015
O	-1.22781	7.20526	1.01194
C	-0.26178	9.38377	1.18754
C	1.02124	7.32151	1.95288
H	-1.20572	-6.11718	4.63081
H	-0.14085	-5.81261	2.41781
H	-2.7483	-2.10977	4.41388
H	-2.51553	-4.24601	5.64117
H	0.74384	-6.22978	-1.14149
H	1.94728	-6.90099	-3.19825
H	3.07929	-5.16866	-4.59248
H	3.00141	-2.79135	-3.90207
H	1.82657	3.31046	0.97353
H	1.26535	3.64697	-3.27798
H	1.50418	1.2099	-3.49713
H	-2.5042	1.58452	3.4201
H	-3.00783	3.96889	2.93215
H	-2.83991	3.12494	-1.27855
H	1.24836	6.26622	-2.49367
H	-0.10065	5.11308	-2.413
H	-3.17062	6.67805	-0.54488
H	-2.53847	5.22325	-1.33645
H	-0.67122	5.27355	0.47048
H	-0.91475	7.27873	-1.80906
H	-0.68108	9.54203	2.18488
H	0.66404	9.95873	1.10446
H	-0.97396	9.74395	0.44148
H	0.65136	7.43087	2.97611
H	1.19008	6.26282	1.74304
H	1.97835	7.84384	1.86921
C	2.20458	0.6751	1.03943
C	2.46954	0.02839	2.03536
C	2.73827	-0.71162	3.22158
C	3.60501	-1.84181	3.20468
H	4.47812	-3.41656	4.38008
C	3.81905	-2.55508	4.39902
C	3.20695	-2.16432	5.58578
C	2.36466	-1.04812	5.60429
H	1.88638	-0.73939	6.52842
C	2.13352	-0.33157	4.4346
H	1.47458	0.5301	4.44008
C	-2.33416	0.54521	-1.07941
C	-2.24128	-0.22886	-2.01363
C	-2.07883	-1.12001	-3.1119
C	-1.41539	-0.68387	-4.27427
H	-1.0511	0.33725	-4.31264

H	-0.70224	-1.18657	-6.2368	H	6.90244	5.56142	0.63103
C	-1.21874	-1.54243	-5.35096	C	5.90402	3.71103	1.11406
C	-1.68168	-2.86047	-5.28723	H	5.28129	4.15511	1.88482
C	-2.34627	-3.31092	-4.15099	C	-3.27575	-2.93715	-1.91554
H	-2.71409	-4.33013	-4.09934	C	-3.91618	-3.36994	-0.97576
C	-2.5634	-2.4582	-3.05245	C	-4.64466	-3.91222	0.12184
H	-1.52748	-3.53498	-6.12348	C	-4.28765	-5.17032	0.64223
H	3.38797	-2.72765	6.49574	H	-3.45106	-5.69834	0.19752
C	4.26304	-2.25049	2.00912	C	-4.98367	-5.72779	1.70999
C	4.85403	-2.61685	1.01063	H	-4.68843	-6.69752	2.09784
C	5.53561	-3.09086	-0.14713	C	-6.05835	-5.038	2.28044
C	5.48845	-4.45954	-0.47193	C	-6.43216	-3.79536	1.78002
H	4.91965	-5.12641	0.16708	H	-7.26682	-3.25707	2.2166
C	6.15001	-4.95351	-1.59169	C	-5.74204	-3.2103	0.70067
H	6.09779	-6.01231	-1.82447	C	-6.15656	-1.94562	0.19844
C	6.87878	-4.0864	-2.41219	C	-6.53976	-0.86861	-0.21913
C	6.94207	-2.73036	-2.10928	C	-6.98166	0.38978	-0.72175
H	7.50786	-2.0535	-2.74076	C	-6.23441	1.06687	-1.70766
C	6.27949	-2.20692	-0.98209	H	-5.31184	0.62468	-2.06868
C	6.37224	-0.81836	-0.68757	C	-8.17389	0.9733	-0.24578
C	6.47585	0.37138	-0.4532	H	-8.75161	0.45622	0.51345
C	6.58882	1.76292	-0.16585	C	-8.6045	2.19911	-0.74646
C	5.78718	2.35207	0.83375	H	-9.52431	2.63858	-0.37247
H	5.07605	1.73559	1.37361	C	-7.85895	2.8617	-1.72553
C	7.504	2.56928	-0.8734	H	-8.1984	3.81702	-2.1142
H	8.12241	2.11988	-1.64363	C	-6.67489	2.29186	-2.20193
C	7.61257	3.92706	-0.58466	H	-6.09248	2.80434	-2.96182
H	8.32118	4.53819	-1.13557	H	7.39752	-4.46759	-3.28619
C	6.81513	4.50225	0.40872	H	-6.60426	-5.4693	3.11363

Low frequencies --- 6.2544 6.9614 8.6643 -3570.890784

Zero-point correction= 1.271434 (Hartree/Particle)

Thermal correction to Energy= 1.00092

Thermal correction to Enthalpy= 1.0112929

Thermal correction to Gibbs Free Energy= 1.00043

Sum of electronic and zero-point Energies= -3569.61935

Sum of electronic and thermal Energies= -3569.88986

Sum of electronic and thermal Enthalpies= -3569.87949

Sum of electronic and thermal Free Energies= -3569.89035

Table S17. Atomic coordinates for the DFT optimized structure of (*S*,*S*,*P*)-**5**

	X	Y	Z				
C	0.89023	-4.83765	4.77723	C	0.52587	-3.63424	2.68258
C	0.94859	-4.77985	3.39034	C	0.02111	-2.52474	3.41617
				C	-0.02328	-2.60543	4.82437
				C	0.40355	-3.74263	5.49882

C	0.62939	-3.66494	1.26158	H	-3.02406	2.91439	-0.19015
C	-0.44921	-1.32575	2.80783	H	0.36083	6.01293	-3.12051
C	0.79384	-3.86523	0.07131	H	-0.84309	4.8662	-2.49478
C	0.96281	-4.27874	-1.28177	H	-3.08039	6.52972	0.25503
C	0.91145	-5.65896	-1.56663	H	-2.71035	5.01167	-0.58497
C	1.06227	-6.13372	-2.86441	H	-0.32347	5.25188	0.39956
C	1.27116	-5.23495	-3.91574	H	-1.45442	7.05874	-1.77743
C	1.32978	-3.86993	-3.65923	H	0.10824	9.65042	1.66717
C	1.18292	-3.36585	-2.35136	H	0.96296	9.9828	0.14763
C	1.25512	-1.96161	-2.13999	H	-0.79405	9.6968	0.13442
C	1.33056	-0.75157	-2.03515	H	1.71804	7.62472	2.09082
C	-0.89738	-0.25033	2.45266	H	1.82925	6.3619	0.83849
C	-1.36401	1.06091	2.15511	H	2.54543	7.95622	0.55395
C	1.32897	0.66678	-1.94573	C	2.49291	0.636	0.24321
C	1.85745	1.35053	-0.81108	C	3.05351	0.0389	1.14242
C	1.73661	2.74453	-0.73067	C	3.6712	-0.65058	2.22332
C	1.11667	3.47219	-1.75008	C	4.45881	-1.81724	2.0023
C	0.65279	2.81387	-2.89791	H	5.6192	-3.36923	2.93443
C	0.75877	1.42952	-2.97965	C	5.02246	-2.48021	3.10869
C	-1.14114	2.09153	3.09059	C	4.82941	-2.006	4.40198
C	-1.56084	3.39172	2.85045	C	4.06618	-0.8542	4.61792
C	-2.22521	3.70236	1.65675	H	3.91527	-0.47961	5.6254
C	-2.47585	2.69886	0.71891	C	3.49494	-0.18562	3.54024
C	-2.05937	1.37633	0.95474	H	2.89519	0.70372	3.70144
O	-2.66472	4.99673	1.50971	C	-2.37929	0.36418	0.00285
O	1.01691	4.81974	-1.55109	C	-2.7048	-0.48396	-0.80558
C	-0.02872	5.54184	-2.21136	C	-3.06249	-1.47289	-1.76796
C	-2.4286	5.65335	0.25676	C	-2.55414	-1.39452	-3.07706
C	-0.97767	6.0879	0.12193	H	-1.89441	-0.57168	-3.32949
C	-0.58527	6.60556	-1.27342	H	-2.47474	-2.27735	-5.0335
O	0.38669	7.61142	-1.00312	C	-2.87971	-2.35535	-4.02949
C	0.38765	7.91845	0.40666	C	-3.72293	-3.41796	-3.69137
O	-0.72763	7.21622	0.9575	C	-4.24005	-3.51354	-2.4033
C	0.1508	9.40921	0.6015	H	-4.89943	-4.33263	-2.13705
C	1.70289	7.43268	1.01438	C	-3.92823	-2.55078	-1.42551
H	1.22421	-5.73166	5.29435	H	-3.9782	-4.17006	-4.43113
H	1.3291	-5.62333	2.82421	H	5.27534	-2.53147	5.24049
H	-0.40793	-1.75477	5.37674	C	4.69152	-2.31146	0.68747
H	0.35461	-3.77712	6.58264	C	4.91866	-2.74245	-0.42784
H	0.74462	-6.35033	-0.7474	C	5.14501	-3.28134	-1.72635
H	1.01556	-7.20102	-3.05665	C	5.14038	-4.67677	-1.91338
H	1.38927	-5.59828	-4.93176	H	4.97601	-5.31635	-1.05283
H	1.4976	-3.16756	-4.46866	C	5.32972	-5.23098	-3.17501
H	2.11287	3.27147	0.13852	H	5.31915	-6.30947	-3.29648
H	0.2122	3.36597	-3.71953	C	5.52861	-4.39929	-4.28162
H	0.38498	0.91735	-3.86001	C	5.54341	-3.01765	-4.11964
H	-0.61777	1.85514	4.01079	H	5.70467	-2.36759	-4.97311
H	-1.37819	4.1816	3.57082	C	5.35987	-2.43396	-2.85171

C	5.40451	-1.01634	-2.71604	H	-6.94286	5.43965	-0.18788
C	5.47242	0.19633	-2.64041	C	-7.26299	3.33743	-0.48652
C	5.52876	1.61859	-2.58367	H	-7.72703	3.46301	-1.45914
C	6.31059	2.28848	-1.59768	H	5.67519	-4.82747	-5.26821
C	4.80982	2.38354	-3.52129	H	-6.81944	-3.36064	5.95065
H	4.21639	1.86736	-4.26828	C	-7.58479	0.91817	-0.71755
C	4.84686	3.77395	-3.49063	C	-7.99538	-0.02557	-1.36709
H	4.28195	4.34429	-4.22108	C	-8.47271	-1.14328	-2.11191
C	5.60929	4.43181	-2.51996	C	-9.26972	-0.95441	-3.25962
H	5.63998	5.51641	-2.49186	H	-9.51547	0.05435	-3.57528
C	6.33265	3.69661	-1.58689	C	-9.7375	-2.05182	-3.97779
H	6.92885	4.20165	-0.83426	H	-10.3514	-1.89432	-4.85948
C	-4.48064	-2.66056	-0.11661	C	-9.42105	-3.34981	-3.56723
C	-4.96474	-2.75881	0.99564	H	-9.78869	-4.20301	-4.12919
C	-5.48712	-2.90655	2.3133	C	-8.62994	-3.54666	-2.43179
C	-5.41449	-4.1558	2.95763	H	-8.3816	-4.5537	-2.11013
H	-4.97072	-4.99076	2.42594	C	-8.1563	-2.45653	-1.70636
C	-5.89048	-4.32112	4.25448	C	7.07596	1.56054	-0.64498
H	-5.82166	-5.29267	4.73346	C	7.75264	0.96125	0.16995
C	-6.44978	-3.23687	4.93767	C	8.54646	0.24367	1.11144
C	-6.53773	-1.99423	4.31794	C	9.45627	0.92272	1.9478
H	-6.97737	-1.1512	4.84035	H	9.54294	2.00179	1.87233
C	-6.06924	-1.80502	3.00422	C	10.23564	0.21459	2.85876
C	-6.19891	-0.52808	2.38474	H	10.93347	0.74811	3.49709
C	-6.34958	0.56798	1.87829	C	10.12282	-1.17542	2.95202
C	-6.51319	1.86391	1.30925	H	10.73301	-1.72431	3.66289
C	-7.11916	2.03533	0.0301	C	9.22202	-1.85676	2.12859
C	-6.07839	2.99951	2.01733	H	9.13066	-2.93652	2.19923
H	-5.61555	2.86183	2.98855	C	8.43739	-1.15865	1.21428
C	-6.22722	4.2766	1.48495	H	-7.53601	-2.60444	-0.82864
H	-5.87474	5.13671	2.04443	H	7.7316	-1.68268	0.57849
C	-6.82194	4.44523	0.2303				

Low frequencies --- 6.3185 7.0364 8.344
-4185.329809
Zero-point correction= 1.271431 (Hartree/Particle)
Thermal correction to Energy= 1.360925
Thermal correction to Enthalpy= 1.361869
Thermal correction to Gibbs Free Energy= 1.126746
Sum of electronic and zero-point Energies= -4184.058378
Sum of electronic and thermal Energies= -4183.968884
Sum of electronic and thermal Enthalpies= -4183.96794
Sum of electronic and thermal Free Energies= -4184.203063

Table S18. Atomic coordinates for the DFT optimized structure of (*S,S,P*)-**6**

	X	Y	Z
C	-0.69531	-4.32082	4.343465
C	-0.38007	-4.24173	2.992577
C	-0.56317	-3.04789	2.262868
C	-1.09226	-1.91054	2.934448
C	-1.3991	-2.01369	4.307663
C	-1.20604	-3.19946	5.005444
C	-0.20927	-3.0589	0.882138
C	-1.33117	-0.66341	2.290695
C	0.150067	-3.25011	-0.26592
C	0.525896	-3.64777	-1.5816
C	0.349559	-4.99935	-1.94322
C	0.698355	-5.45934	-3.20778
C	1.23736	-4.57414	-4.14722
C	1.424002	-3.23786	-3.8128
C	1.080357	-2.7493	-2.53614
C	1.296098	-1.37443	-2.24366
C	1.509856	-0.18861	-2.07331
C	-1.59484	0.450535	1.875422
C	-1.8566	1.794854	1.490161
C	1.675954	1.215016	-1.92707
C	2.024286	1.807031	-0.67681
C	2.067161	3.203393	-0.56555
C	1.786709	4.020718	-1.66415
C	1.511748	3.444772	-2.91274
C	1.451896	2.060194	-3.0272
C	-1.72789	2.82068	2.447039
C	-1.94619	4.150685	2.11625
C	-2.30555	4.494531	0.806879
C	-2.45627	3.499237	-0.15994
C	-2.24328	2.147256	0.164977
O	-2.57106	5.821106	0.556304
O	1.815656	5.366875	-1.4324
C	1.053364	6.236732	-2.27648
C	-1.91169	6.439968	-0.55673
C	-0.4557	6.746666	-0.24539
C	0.356014	7.2944	-1.4315
O	1.303641	8.162477	-0.81687
C	0.900458	8.434011	0.541309
O	-0.37477	7.808974	0.702679
C	0.7189	9.93353	0.730664
C	1.935337	7.827297	1.487493
H	-0.54177	-5.25221	4.879403
H	0.021055	-5.10588	2.473808
H	-1.80083	-1.14164	4.812443
H	-1.45456	-3.25093	6.060841
H	-0.07139	-5.67995	-1.21073
H	0.550266	-6.50447	-3.46094
H	1.512728	-4.92603	-5.1365
H	1.847161	-2.54702	-4.53415
H	2.305601	3.664504	0.385869
H	1.34278	4.060276	-3.78823
H	1.21447	1.613924	-3.98706
H	-1.43811	2.556466	3.458408
H	-1.8376	4.937469	2.85474
H	-2.77053	3.751162	-1.16611
H	1.716368	6.717426	-3.00389
H	0.290126	5.675318	-2.82507
H	-2.45642	7.368413	-0.74282
H	-1.97805	5.811504	-1.45217
H	0.030105	5.843946	0.146952
H	-0.29425	7.872436	-2.10858
H	0.368652	10.14839	1.743975
H	1.668399	10.45173	0.573753
H	-0.01558	10.30971	0.014614
H	1.646576	8.000681	2.527829
H	2.021963	6.752001	1.314181
H	2.914841	8.282311	1.315911
C	2.314826	0.995016	0.4552
C	2.581967	0.290124	1.409754
C	2.841331	-0.52334	2.548035
C	3.485447	-1.78812	2.41994
H	4.169441	-3.53655	3.467933
C	3.680058	-2.57404	3.571549
C	3.263817	-2.12818	4.82162
C	2.643206	-0.8812	4.949093
H	2.318116	-0.52932	5.923112
C	2.436305	-0.08896	3.824559
H	1.945905	0.874456	3.914252
C	-2.44693	1.140362	-0.82003
C	-2.63339	0.266128	-1.64482
C	-2.82111	-0.75817	-2.61423
C	-2.38866	-0.55948	-3.93887
H	-1.92778	0.387615	-4.19867
H	-2.18841	-1.3863	-5.91096
C	-2.53295	-1.55848	-4.89612
C	-3.11492	-2.78168	-4.54787
C	-3.55551	-2.99766	-3.2463
H	-4.01426	-3.94172	-2.97261
C	-3.42601	-1.99951	-2.26193
H	-3.22619	-3.56522	-5.29067
H	3.425064	-2.75041	5.6962
C	3.940722	-2.26032	1.156766

C	4.356633	-2.68404	0.094846
C	4.811921	-3.20479	-1.14869
C	4.680579	-4.57905	-1.42408
H	4.240574	-5.2212	-0.66869
C	5.094003	-5.10764	-2.64253
H	4.980851	-6.16989	-2.83459
C	5.65011	-4.27141	-3.61604
C	5.795856	-2.91125	-3.36366
H	6.232431	-2.25857	-4.11227
C	5.389612	-2.35493	-2.13599
C	5.566152	-0.96302	-1.895
C	5.734489	0.226954	-1.70239
C	5.876541	1.631849	-1.52081
C	6.221754	2.18614	-0.25498
C	5.652119	2.498406	-2.60795
H	5.391292	2.069145	-3.56939
C	5.748608	3.877548	-2.4568
H	5.568916	4.526808	-3.3078
C	6.070677	4.42316	-1.20994
H	6.142546	5.498961	-1.08577
C	6.30469	3.585817	-0.1241
H	6.564124	4.002888	0.843165
C	-3.90595	-2.24253	-0.94391
C	-4.34564	-2.482	0.165156
C	-4.81123	-2.81318	1.469159
C	-4.63855	-4.12293	1.956236
H	-4.16392	-4.85744	1.31452
C	-5.05605	-4.47321	3.235888
H	-4.91016	-5.48856	3.590661
C	-5.65747	-3.51801	4.061627
C	-5.84337	-2.21918	3.600371
H	-6.31557	-1.47531	4.233296
C	-5.43374	-1.84307	2.306858
C	-5.65956	-0.51152	1.857034
C	-5.88335	0.630112	1.499244
C	-6.11265	1.979231	1.105621
C	-6.47116	2.308135	-0.23377
C	-5.97183	3.01538	2.048312
H	-5.7019	2.758675	3.0671
C	-6.15951	4.345017	1.685201
H	-6.04114	5.127976	2.427352
C	-6.49235	4.669504	0.366214
H	-6.6356	5.705977	0.077792
C	-6.64776	3.661308	-0.57988
H	-6.91802	3.905738	-1.60177
H	5.972601	-4.68031	-4.56838
H	-5.9835	-3.78661	5.061473
C	-6.67577	1.297458	-1.21684
C	-6.89422	0.465492	-2.07755
C	-7.13944	-0.48441	-3.11043
C	-6.56605	-0.29741	-4.38208
H	-5.93271	0.567982	-4.54503
C	-6.79513	-1.20435	-5.41187
H	-6.34021	-1.0419	-6.38378
C	-7.60869	-2.32062	-5.1922
H	-7.7907	-3.03045	-5.99298
C	-8.18928	-2.5241	-3.94481
H	-8.82387	-3.38644	-3.76971
C	-7.97156	-1.62034	-2.88688
C	-8.59311	-1.84264	-1.62689
C	-9.14746	-2.04779	-0.56306
C	-9.79754	-2.27341	0.685132
C	-9.50621	-1.45885	1.798882
C	-10.7449	-3.30871	0.823308
C	-10.1506	-1.67718	3.013834
C	-11.3828	-3.51848	2.043075
C	-11.0898	-2.7045	3.140865
H	-8.77095	-0.66763	1.697705
H	-10.9717	-3.93827	-0.03098
H	-12.1111	-4.31833	2.13753
H	-11.5902	-2.87042	4.090109
H	-9.91936	-1.04366	3.864948
C	6.504077	1.361951	0.872891
C	6.793699	0.723365	1.867577
C	7.116304	0.016057	3.061394
C	6.54815	0.4195	4.284412
H	5.857786	1.256066	4.28635
C	6.855005	-0.24113	5.46968
H	6.403187	0.085748	6.40083
C	7.742677	-1.3219	5.458139
H	7.985606	-1.83972	6.380693
C	8.319367	-1.73591	4.262121
H	9.011354	-2.57134	4.247478
C	8.02375	-1.08306	3.049727
C	8.642818	-1.51493	1.844261
C	9.195796	-1.89719	0.829794
C	9.839848	-2.33004	-0.36573
C	9.442781	-1.81421	-1.61675
C	10.88507	-3.27525	-0.31521
C	10.07988	-2.23467	-2.78134
C	11.51499	-3.68865	-1.48608
C	11.11648	-3.17041	-2.72148
H	8.633375	-1.09299	-1.65901
H	11.19324	-3.67506	0.645421
H	12.31928	-4.41638	-1.43491
H	11.61061	-3.49462	-3.63233

H	9.766516	-1.83118	-3.73956

Low frequencies --- 8.2673 9.13 9.3077
-4799.768101
Zero-point correction= 1.454385 (Hartree/Particle)
Thermal correction to Energy= 1.55625
Thermal correction to Enthalpy= 1.557195
Thermal correction to Gibbs Free Energy= 1.300958
Sum of electronic and zero-point Energies= -4798.313716
Sum of electronic and thermal Energies= -4798.21185
Sum of electronic and thermal Enthalpies= -4798.210906
Sum of electronic and thermal Free Energies= -4798.467143

Table S19. Atomic coordinates for the DFT optimized structure of (*S,S,P*)-**1:Ag**

	X	Y	Z
C	6.515357	-3.11039	-0.40135
C	6.265615	-1.76875	-0.15695
C	4.956231	-1.26743	-0.18599
C	3.885002	-2.14532	-0.47733
C	4.158399	-3.49867	-0.71856
C	5.459671	-3.97694	-0.68
C	4.769345	0.1186	0.087121
C	2.522013	-1.71923	-0.54212
C	4.759838	1.315806	0.351504
C	4.919208	2.703103	0.63519
C	6.221599	3.22192	0.673502
C	6.440643	4.565906	0.935217
C	5.361801	5.41849	1.163173
C	4.066731	4.923083	1.134147
C	3.824401	3.567633	0.874841
C	2.468075	3.12031	0.868469
C	1.257927	2.944539	0.954286
C	1.313051	-1.59195	-0.71481
C	-0.09753	-1.56775	-0.88964
C	-0.15359	2.78574	1.008764
C	-0.97906	3.677074	0.303445
C	-2.35521	3.530444	0.283896
C	-2.94324	2.474702	0.986208
C	-2.1491	1.5718	1.701138
C	-0.77724	1.733632	1.706175
C	-0.79474	-0.51567	-1.50353
C	-2.17356	-0.53125	-1.6603
C	-2.89596	-1.65057	-1.23085
C	-2.22349	-2.71651	-0.61826
C	-0.85676	-2.66988	-0.4469
O	-4.22344	-1.81603	-1.40043
O	-4.2732	2.264039	1.033046
C	-5.0452	2.479979	-0.14408
C	-5.0679	-0.68371	-1.56097
C	-5.34619	-0.04622	-0.22128
C	-6.01758	1.328914	-0.29602
O	-6.95751	1.314288	0.752866
C	-6.96073	0.030565	1.381129
O	-6.27991	-0.82953	0.484096
C	-8.38469	-0.45059	1.513794
C	-6.24225	0.113439	2.714117
H	7.536572	-3.48292	-0.37297
H	7.083167	-1.08624	0.064745
H	3.329764	-4.16816	-0.93875
H	5.650846	-5.03045	-0.8702
H	7.058264	2.550664	0.492081
H	7.457602	4.95012	0.960349
H	5.52986	6.473366	1.366951
H	3.219629	5.580883	1.31586
H	-2.97267	4.240748	-0.26078
H	-2.62482	0.74632	2.226621
H	-2.65732	0.311804	-2.14514
H	-2.80478	-3.57154	-0.28247
H	-5.58666	3.431292	-0.06273
H	-4.38869	2.52752	-1.02689
H	-6.00158	-1.06677	-1.98677
H	-4.64627	0.039414	-2.27341
H	-4.39658	0.029598	0.340045
H	-6.5431	1.456189	-1.26056
H	-8.40864	-1.44745	1.969287
H	-8.95461	0.23698	2.149133
H	-8.85375	-0.4973	0.524854
H	-6.2147	-0.87449	3.189239
H	-5.21794	0.480016	2.579588

H	-6.76748	0.808773	3.38002	Br	0.159977	0.999165	-2.1723
H	-0.51183	4.494902	-0.24116	H	-0.34006	-3.49607	0.036647
Br	0.280519	0.41712	2.602472	Ag	2.267493	0.659649	0.206466

Low frequencies --- -7.7651 -0.0008 0.0003 0.0009 6.7121 10.1859
Low frequencies --- 16.9079 23.6756 29.4802
Zero-point correction= 0.527201 (Hartree/Particle)
Thermal correction to Energy= 0.566685
Thermal correction to Enthalpy= 0.567629
Thermal correction to Gibbs Free Energy= 0.453022
Sum of electronic and zero-point Energies= -1896.526921
Sum of electronic and thermal Energies= -1896.487437
Sum of electronic and thermal Enthalpies= -1896.486493
Sum of electronic and thermal Free Energies= -1896.601100

Table S20. Atomic coordinates for the DFT optimized structure of (*S,S,P*)-**2:Ag**

	X	Y	Z				
C	-5.79689	4.077409	-1.24945	O	4.381882	0.485006	-3.03521
C	-5.60148	2.864146	-0.60715	O	4.459649	-1.34612	1.448549
C	-4.38644	2.174288	-0.72885	C	5.09303	-2.27023	0.57179
C	-3.35407	2.727005	-1.52517	C	5.078867	-0.61638	-2.47276
C	-3.57138	3.957227	-2.16224	C	5.453576	-0.32862	-1.04
C	-4.77924	4.62493	-2.02875	C	6.075855	-1.51594	-0.29813
C	-4.26204	0.939055	-0.02528	O	7.105853	-0.942	0.473576
C	-2.08496	2.103663	-1.70146	C	7.198672	0.455279	0.18786
C	-4.34191	-0.08385	0.647321	O	6.47498	0.64144	-1.01546
C	-4.64944	-1.27844	1.363592	C	8.641819	0.814009	-0.06616
C	-5.99303	-1.67945	1.404377	C	6.58605	1.250113	1.325189
C	-6.36508	-2.84721	2.05323	H	-6.74638	4.596976	-1.14215
C	-5.39996	-3.63571	2.677211	H	-6.38866	2.431797	0.007183
C	-4.06775	-3.25137	2.654885	H	-2.77156	4.377222	-2.76884
C	-3.67086	-2.07317	2.007508	H	-4.92733	5.576913	-2.53352
C	-2.28416	-1.75212	1.989787	H	-6.73827	-1.06101	0.908046
C	-1.06991	-1.61961	2.032413	H	-7.4112	-3.14402	2.070709
C	-0.95272	1.710603	-1.94923	H	-5.68659	-4.55456	3.183811
C	0.392231	1.342753	-2.22455	H	-3.30815	-3.86201	3.139011
C	0.348315	-1.54045	1.982576	H	2.912123	0.6748	1.505671
C	1.010065	-0.29741	1.814675	H	3.057629	-3.60947	1.827436
C	2.394748	-0.27141	1.655903	H	0.600605	-3.66948	2.136751
C	3.125183	-1.45779	1.637313	H	0.948969	3.340061	-2.80291
C	2.482597	-2.68614	1.818572	H	3.323742	2.751049	-3.26852
C	1.108788	-2.71692	1.99743	H	2.529299	-1.31608	-2.1019
C	1.300019	2.318933	-2.6666	H	5.613093	-3.04264	1.15395
C	2.618306	1.999951	-2.92133	H	4.343584	-2.76384	-0.06917
C	3.083647	0.69244	-2.7218	H	5.988451	-0.72734	-3.07333
C	2.204831	-0.292	-2.27003	H	4.50308	-1.54973	-2.55729
C	0.857622	0.017797	-2.04757	H	4.559813	0.03312	-0.49852
				H	6.511459	-2.23626	-1.01579

H	8.729045	1.876394	-0.32215	H	0.567129	4.070389	0.233259
H	9.241003	0.620826	0.830933	C	-0.04888	-1.01321	-1.66637
H	9.031228	0.212561	-0.89492	C	-0.83636	-1.91705	-1.43326
H	6.638154	2.323527	1.10684	C	-1.7552	-2.96951	-1.14457
H	5.539635	0.96181	1.479114	C	-1.31441	-4.14063	-0.50972
H	7.133414	1.054284	2.255118	H	-0.25642	-4.2534	-0.27666
C	0.268241	0.913272	1.705321	H	-1.88164	-6.03637	0.322314
C	-0.34115	1.963509	1.580849	C	-2.22643	-5.13191	-0.17485
C	-1.03462	3.194075	1.382978	C	-3.57932	-4.96777	-0.46956
C	-2.33371	3.36788	1.884839	C	-4.02016	-3.81608	-1.11703
H	-2.79217	2.568542	2.467117	H	-5.07465	-3.69223	-1.35559
H	-4.04009	4.666109	1.99998	C	-3.11569	-2.81905	-1.45639
C	-3.02866	4.539699	1.618726	H	-3.45152	-1.91096	-1.95743
C	-2.4362	5.546128	0.859503	H	-4.29187	-5.74458	-0.19849
C	-1.13941	5.385736	0.372264	H	-2.98617	6.461437	0.648708
H	-0.67711	6.17513	-0.21709	Ag	-1.81378	0.156572	0.099853
C	-0.43785	4.21602	0.627302				

Low frequencies --- -11.9715 -6.0811 -0.0046 -0.0028 -0.0013 4.9028
Low frequencies --- 21.4961 24.6303 29.3888
Zero-point correction= 0.730185 (Hartree/Particle)
Thermal correction to Energy= 0.779384
Thermal correction to Enthalpy= 0.780328
Thermal correction to Gibbs Free Energy= 0.648063
Sum of electronic and zero-point Energies= -2485.186268
Sum of electronic and thermal Energies= -2485.137069
Sum of electronic and thermal Enthalpies= -2485.136125
Sum of electronic and thermal Free Energies= -2485.268390

Table S21. Atomic coordinates for the DFT optimized structure of (*S,S,P*)-**3:Ag**

	X	Y	Z				
C	-4.42783	3.94565	2.969471	C	-0.50986	-2.17963	-0.60142
C	-4.40813	2.729497	2.304994	C	0.190513	2.711984	0.382468
C	-3.27665	2.319517	1.58367	C	1.557231	2.664567	-0.01343
C	-2.14322	3.166249	1.539843	C	0.907155	-2.2313	-0.51755
C	-2.18662	4.39612	2.21403	C	1.590559	-1.53207	0.511541
C	-3.31419	4.782776	2.921446	C	2.983767	-1.49105	0.509242
C	-3.35235	1.072518	0.897278	C	3.704978	-2.12859	-0.49791
C	-0.93051	2.833967	0.86523	C	3.040844	-2.84146	-1.50104
C	-3.57096	0.000523	0.346214	C	1.65531	-2.89577	-1.49725
C	-4.01779	-1.17467	-0.32645	C	2.483746	3.437966	0.708505
C	-5.39991	-1.33226	-0.507	C	3.829312	3.416049	0.403765
C	-5.90825	-2.43352	-1.17989	C	4.306906	2.601905	-0.63301
C	-5.04225	-3.3991	-1.69066	C	3.408625	1.826883	-1.36345
C	-3.67294	-3.26278	-1.52078	C	2.037242	1.865086	-1.07666
C	-3.13991	-2.16261	-0.83621	O	5.637254	2.665054	-0.86402
C	-1.72568	-2.08373	-0.68993	O	5.05296	-2.04122	-0.42391
				C	5.787057	-1.82755	-1.62184

C	6.279242	1.597779	-1.5477
C	6.470757	0.416683	-0.62734
C	6.922766	-0.87037	-1.32501
O	7.85177	-1.44027	-0.43109
C	8.054373	-0.5601	0.676671
O	7.525477	0.688327	0.266776
C	9.535093	-0.39172	0.912046
C	7.320892	-1.09574	1.891098
H	-5.31529	4.243312	3.523688
H	-5.27482	2.071607	2.330258
H	-1.31318	5.044428	2.169608
H	-3.32441	5.740817	3.436455
H	-6.0688	-0.56854	-0.11451
H	-6.98306	-2.53513	-1.31263
H	-5.43614	-4.2625	-2.22252
H	-2.98652	-4.00836	-1.91803
H	3.517756	-0.94242	1.283728
H	3.608426	-3.36114	-2.27023
H	1.129933	-3.44379	-2.27721
H	2.122898	4.058101	1.527047
H	4.544162	4.013052	0.965061
H	3.733024	1.186629	-2.17991
H	6.182843	-2.7797	-2.00098
H	5.135049	-1.39084	-2.39633
H	7.257095	1.986673	-1.85244
H	5.732945	1.313955	-2.45895
H	5.530883	0.230813	-0.07583
H	7.42705	-0.63888	-2.28161
H	9.70982	0.306786	1.738813
H	9.988499	-1.35624	1.167578
H	10.01006	-0.0003	0.005662
H	7.441785	-0.41051	2.738784
H	6.253545	-1.21936	1.673272
H	7.726901	-2.0755	2.170369
C	0.855077	-0.83921	1.51101
C	0.219253	-0.26411	2.376163
C	-0.54624	0.39995	3.373203
C	-1.79558	-0.13528	3.779789
H	-3.52191	0.162881	5.022545
C	-2.56012	0.570896	4.71735
C	-2.09644	1.763185	5.256045
C	-0.86073	2.279219	4.865021
H	-0.50219	3.216438	5.285519
C	-0.09087	1.602104	3.930139
H	0.864156	2.006053	3.595427
C	1.168815	1.081145	-1.8875
C	0.525884	0.407064	-2.67664
C	-0.24554	-0.44389	-3.51481
C	0.361629	-1.50701	-4.19442
H	1.444041	-1.61363	-4.14626
H	0.071734	-3.25268	-5.40973
C	-0.41007	-2.42524	-4.89335
C	-1.79809	-2.29155	-4.92662
C	-2.41426	-1.22054	-4.29297
H	-3.49547	-1.09857	-4.33088
C	-1.65191	-0.27714	-3.5956
H	-2.40299	-3.02083	-5.46119
H	-2.70596	2.299184	5.98073
C	-2.25389	-1.36399	3.233613
C	-2.60511	-2.41508	2.733989
C	-2.95989	-3.65129	2.123947
C	-4.30314	-4.02782	1.976214
H	-5.08481	-3.35769	2.331503
C	-4.62519	-5.23363	1.368133
H	-5.66989	-5.51766	1.253408
C	-3.61751	-6.07332	0.897561
C	-2.28048	-5.70264	1.033873
H	-1.49256	-6.35739	0.666114
C	-1.94942	-4.50011	1.642931
C	-2.25586	0.842416	-2.96355
C	-2.71522	1.86088	-2.478
C	-3.18648	3.081018	-1.9188
C	-4.50998	3.214087	-1.47344
H	-5.19077	2.368617	-1.56843
C	-4.93008	4.406484	-0.89983
H	-5.95523	4.50549	-0.5479
C	-4.04047	5.471371	-0.76615
C	-2.72701	5.348629	-1.21571
H	-2.03271	6.180108	-1.1097
C	-2.29751	4.160766	-1.78936
H	-3.87465	-7.01811	0.421841
H	-4.37326	6.400335	-0.30649
H	-1.27098	4.044732	-2.136
H	-0.90829	-4.19821	1.755453
Ag	-1.08115	0.502226	-0.26781

Low frequencies --- -3.8072 -0.0047 -0.0037 -0.0023 4.7135 8.3621
Low frequencies --- 14.1661 18.2149 21.9943
Zero-point correction= 0.911165 (Hartree/Particle)
Thermal correction to Energy= 0.973938
Thermal correction to Enthalpy= 0.974882

Thermal correction to Gibbs Free Energy= 0.811971
Sum of electronic and zero-point Energies= -3098.960532
Sum of electronic and thermal Energies= -3098.897759
Sum of electronic and thermal Enthalpies= -3098.896815
Sum of electronic and thermal Free Energies= -3099.059726

Table S22. Atomic coordinates for the DFT optimized structure of (*S,S,P*)-**4:Ag$_2$**

	X	Y	Z
C	-3.98271	0.796571	4.35289
C	-4.04596	0.514887	2.994573
C	-2.89892	0.603784	2.197649
C	-1.67462	1.0206	2.778837
C	-1.62807	1.285981	4.152802
C	-2.77093	1.168531	4.932951
C	-2.98083	0.2406	0.82144
C	-0.49858	1.192679	1.991944
C	-3.12546	-0.15653	-0.32792
C	-3.38078	-0.53357	-1.67806
C	-4.68731	-0.45145	-2.17362
C	-4.95673	-0.76697	-3.49869
C	-3.92478	-1.16925	-4.34547
C	-2.625	-1.27153	-3.86712
C	-2.3339	-0.96279	-2.53307
C	-0.99327	-1.0841	-2.06503
C	0.170403	-1.23888	-1.71065
C	0.534608	1.394306	1.36509
C	1.827538	1.616809	0.808049
C	1.568783	-1.41906	-1.50831
C	2.146527	-1.79274	-0.2673
C	3.51806	-2.03205	-0.19352
C	4.335514	-1.91276	-1.32052
C	3.77343	-1.51786	-2.53978
C	2.410259	-1.28341	-2.61893
C	2.92959	1.49554	1.668042
C	4.214251	1.762102	1.226365
C	4.421406	2.164813	-0.09401
C	3.35121	2.258686	-0.97766
C	2.046138	2.000118	-0.5409
O	5.675908	2.520591	-0.48999
O	5.630394	-2.24315	-1.13315
C	6.646638	-1.73038	-1.98726
C	6.377291	1.571378	-1.28292
C	6.721749	0.340697	-0.48793
C	7.500653	-0.72625	-1.24648
O	8.240696	-1.36152	-0.22798
C	8.260299	-0.52744	0.934223
O	7.606916	0.674691	0.556639
C	9.685032	-0.1943	1.30147
C	7.502274	-1.22793	2.043178
H	-4.8809	0.723827	4.961484
H	-4.98646	0.223023	2.530237
H	-0.68282	1.591153	4.597888
H	-2.71734	1.378595	5.998648
H	-5.48516	-0.13477	-1.50356
H	-5.97532	-0.69747	-3.87318
H	-4.13388	-1.40999	-5.38536
H	-1.81519	-1.58739	-4.52247
H	3.966435	-2.3403	0.748843
H	4.371055	-1.43643	-3.44342
H	1.966166	-1.00775	-3.57385
H	2.753146	1.195261	2.700025
H	5.073267	1.680117	1.889645
H	3.52671	2.575995	-2.00426
H	7.260661	-2.57788	-2.31099
H	6.228431	-1.25479	-2.88227
H	7.291321	2.077158	-1.61404
H	5.784716	1.293148	-2.17265
H	5.796054	-0.10521	-0.07795
H	8.183096	-0.25384	-1.97955
H	9.707209	0.47865	2.166764
H	10.23354	-1.10891	1.5539
H	10.17672	0.297227	0.454211
H	7.490119	-0.60729	2.947228
H	6.469972	-1.42708	1.72888
H	7.978734	-2.18673	2.279402
C	1.388052	-1.92999	0.934473
C	0.833861	-2.04956	2.021788
C	0.332365	-2.05655	3.358872
C	-1.01282	-2.36531	3.687479
H	-2.45511	-2.51633	5.27034
C	-1.42071	-2.28397	5.025909
C	-0.52775	-1.91785	6.022379
C	0.796646	-1.62749	5.701034
H	1.501603	-1.344	6.478953
C	1.220682	-1.69608	4.381891
H	2.251834	-1.46521	4.120996
C	0.99392	2.12047	-1.49953

C	0.181097	2.215939	-2.41367	C	2.624546	-5.26142	-1.86965
C	-0.63389	2.166286	-3.5869	H	3.670873	-5.45181	-2.10167
C	-0.01023	1.800488	-4.78877	C	1.743291	-4.8905	-2.88426
H	1.063173	1.620595	-4.78652	H	2.100695	-4.79031	-3.90723
H	-0.24136	1.37415	-6.8784	C	-2.75669	2.768135	-2.4063
C	-0.74443	1.659799	-5.95759	C	-3.51712	3.051646	-1.48972
C	-2.12077	1.876762	-5.9466	C	-4.41062	3.283528	-0.40411
C	-2.75635	2.244727	-4.76976	C	-5.76726	2.963817	-0.54316
H	-3.83253	2.405295	-4.74968	H	-6.12828	2.605003	-1.50521
C	-2.03162	2.40746	-3.58102	C	-6.63631	3.102386	0.530606
H	-2.70275	1.755676	-6.85735	H	-7.68708	2.849939	0.408771
H	-0.8674	-1.86093	7.053908	C	-6.16358	3.558624	1.760303
C	-1.99115	-2.72512	2.712197	C	-4.82409	3.890559	1.914455
C	-2.93807	-3.02098	1.993893	H	-4.44764	4.249826	2.870494
C	-4.04574	-3.26981	1.131122	C	-3.93451	3.768672	0.841518
C	-5.34125	-2.94114	1.549015	C	-2.56192	4.112077	0.999576
H	-5.49047	-2.56599	2.560042	C	-1.39423	4.444981	1.124566
C	-6.41709	-3.08755	0.683659	C	-0.01712	4.798161	1.240237
H	-7.41828	-2.8286	1.020294	C	0.671997	5.294355	0.121718
C	-6.21422	-3.55744	-0.61329	H	0.132514	5.445123	-0.81292
C	-4.93851	-3.8993	-1.04234	C	0.66813	4.596869	2.448225
H	-4.77351	-4.26752	-2.05334	H	0.126957	4.201606	3.307048
C	-3.84358	-3.77309	-0.18118	C	2.023781	4.883703	2.529766
C	-2.53198	-4.1188	-0.61235	H	2.55574	4.720304	3.464949
C	-1.39894	-4.43212	-0.93984	C	2.703473	5.376058	1.416679
C	-0.05105	-4.75668	-1.27314	H	3.768343	5.591052	1.482301
C	0.409095	-4.64065	-2.59342	C	2.027126	5.579912	0.215421
H	-0.2866	-4.33878	-3.37576	H	2.561209	5.958644	-0.65379
C	0.839425	-5.13669	-0.25526	H	-7.05625	-3.66073	-1.29398
H	0.474562	-5.21584	0.768854	H	-6.84477	3.660647	2.602017
C	2.171007	-5.3847	-0.55757	Ag	-1.29728	2.091146	-0.34388
H	2.861364	-5.67043	0.233715	Ag	-1.10761	-1.99256	0.37736

Low frequencies --- -0.0068 -0.0051 -0.0047 3.1021 7.4033 10.8010
Low frequencies --- 20.1451 22.2733 25.3326
Zero-point correction= 1.096889 (Hartree/Particle)
Thermal correction to Energy= 1.173507
Thermal correction to Enthalpy= 1.174451
Thermal correction to Gibbs Free Energy= 0.986024
Sum of electronic and zero-point Energies= -3858.395478
Sum of electronic and thermal Energies= -3858.318860
Sum of electronic and thermal Enthalpies= -3858.317916
Sum of electronic and thermal Free Energies= -3858.506343

Table S23. Atomic coordinates for the DFT optimized structure of (*S,S,P*)-**5:Ag**$_2$

	X	Y	Z				
C	4.137677	-0.42941	-4.11581	C	4.069112	-0.46059	-2.72994
				C	2.875476	-0.1469	-2.06639
				C	1.742748	0.231289	-2.82486

C	1.827438	0.251242	-4.22363
C	3.013674	-0.07784	-4.86361
C	2.857239	-0.18718	-0.64455
C	0.526758	0.641609	-2.20868
C	2.971292	-0.24213	0.568429
C	3.208586	-0.21461	1.971153
C	4.513983	-0.02525	2.444516
C	4.769401	0.039157	3.807561
C	3.724205	-0.08694	4.722531
C	2.427593	-0.29303	4.273243
C	2.154004	-0.36758	2.901426
C	0.821172	-0.61801	2.475854
C	-0.34142	-0.86378	2.189001
C	-0.54502	1.039565	-1.77416
C	-1.8612	1.414074	-1.38097
C	-1.74088	-1.04384	2.021602
C	-2.31721	-1.53408	0.824296
C	-3.70123	-1.6847	0.737595
C	-4.52587	-1.37742	1.821154
C	-3.96112	-0.89273	3.00667
C	-2.58775	-0.72906	3.0918
C	-2.90373	1.307197	-2.31165
C	-4.19528	1.681675	-1.97976
C	-4.47073	2.180297	-0.70457
C	-3.45932	2.264994	0.249305
C	-2.14915	1.903377	-0.0818
O	-5.72523	2.646932	-0.46483
O	-5.84205	-1.62497	1.649651
C	-6.80986	-0.8284	2.323193
C	-6.45262	2.047227	0.597285
C	-6.85683	0.643484	0.237745
C	-7.65282	-0.0886	1.310657
O	-8.44162	-0.98658	0.565264
C	-8.47648	-0.5625	-0.80097
O	-7.75412	0.659501	-0.84809
C	-9.90149	-0.28259	-1.20981
C	-7.79801	-1.62127	-1.64561
H	5.07222	-0.67533	-4.61546
H	4.941282	-0.72846	-2.13435
H	0.948161	0.542818	-4.79635
H	3.063945	-0.05679	-5.94994
H	5.323717	0.070854	1.722158
H	5.787922	0.187342	4.159226
H	3.922007	-0.0291	5.790618
H	1.605327	-0.40406	4.978139
H	-4.15289	-2.05927	-0.17934
H	-4.57737	-0.6775	3.875787
H	-2.14307	-0.36588	4.016768
H	-2.6795	0.934451	-3.30977
H	-5.0102	1.609401	-2.69705
H	-3.66573	2.667263	1.240063
H	-7.43782	-1.48871	2.932473
H	-6.33377	-0.09766	2.990025
H	-7.33806	2.675249	0.746252
H	-5.8654	2.041443	1.531561
H	-5.95105	0.06307	-0.02119
H	-8.29675	0.625833	1.860089
H	-9.93845	0.094691	-2.23818
H	-10.4988	-1.19961	-1.15048
H	-10.3323	0.469743	-0.53804
H	-7.78926	-1.32339	-2.70079
H	-6.76614	-1.76809	-1.30234
H	-8.32802	-2.5765	-1.5527
C	-1.53867	-1.86096	-0.32291
C	-0.98081	-2.17687	-1.36396
C	-0.49927	-2.48513	-2.66906
C	0.796577	-2.99476	-2.91883
H	2.177199	-3.66828	-4.41984
C	1.177533	-3.2769	-4.2386
C	0.30348	-3.0582	-5.29211
C	-0.97276	-2.55214	-5.04688
H	-1.6623	-2.37983	-5.87004
C	-1.36943	-2.27178	-3.74793
H	-2.36578	-1.88228	-3.54477
C	-1.12379	2.110481	0.885871
C	-0.28906	2.373531	1.740099
C	0.538585	2.662331	2.863924
C	-0.06269	2.644366	4.130613
H	-1.12312	2.4079	4.199774
H	0.186089	2.91344	6.245054
C	0.672016	2.930585	5.272261
C	2.027032	3.239744	5.168929
C	2.641304	3.262474	3.925305
H	3.700638	3.496385	3.836627
C	1.915844	2.978825	2.759718
H	2.608022	3.465776	6.060177
H	0.617961	-3.28195	-6.30898
C	1.765116	-3.22804	-1.89936
C	2.734858	-3.46115	-1.18747
C	3.98312	-3.67836	-0.53747
C	5.132734	-3.69617	-1.34191
H	5.018916	-3.5665	-2.41738
C	6.388695	-3.86909	-0.77978
H	7.26908	-3.87917	-1.41815
C	6.518769	-4.02402	0.599828
C	5.393523	-4.0124	1.410871

H	5.487415	-4.13143	2.488317	H	5.148654	3.086394	-3.73428
C	4.114136	-3.84643	0.862641	C	4.239126	3.136904	-1.79027
C	2.989793	-3.84163	1.736149	C	2.969256	3.46008	-2.34714
C	2.11323	-3.88602	2.585666	C	1.945103	3.71408	-2.96244
C	1.071487	-3.86845	3.55422	C	0.735016	3.893195	-3.68754
C	1.338475	-3.48742	4.87469	C	-0.44248	4.335728	-3.03419
H	2.366427	-3.27605	5.164601	C	0.68228	3.551374	-5.04472
C	-0.26202	-4.15802	3.165929	H	1.59485	3.224519	-5.5406
C	-1.294	-4.008	4.09786	C	-0.51775	3.616344	-5.73985
H	-2.31744	-4.21222	3.786845	H	-0.54576	3.347623	-6.79337
C	-1.01354	-3.60518	5.397192	C	-1.68356	4.0166	-5.08724
H	-1.82483	-3.49204	6.11308	H	-2.62576	4.056398	-5.62931
C	0.301955	-3.35743	5.789338	C	-1.64624	4.376605	-3.74656
H	0.519645	-3.05764	6.812176	H	-2.55042	4.696658	-3.2313
C	2.632357	2.99858	1.525482	H	7.502008	-4.15555	1.045792
C	3.395629	3.040363	0.565714	H	7.398765	2.486018	-2.88666
C	4.443098	2.955699	-0.40071	Ag	1.093742	2.6665	-0.48299
C	5.725285	2.627612	0.064676	Ag	0.942396	-2.45729	0.442003
H	5.874975	2.501416	1.13585	C	-0.52746	-4.57253	1.832931
C	6.781317	2.460981	-0.81917	C	-0.70232	-4.97427	0.695781
H	7.766749	2.202893	-0.43833	C	-0.88237	-5.43531	-0.63875
C	6.575848	2.621792	-2.18879	C	-2.11951	-5.28702	-1.28531
C	5.318701	2.959004	-2.66701	H	-2.94953	-4.82983	-0.74787

Low frequencies --- -7.5824 -0.0092 -0.0061 -0.0056 3.5275 7.5907
Low frequencies --- 14.2652 15.8542 19.2653
Zero-point correction= 1.279813 (Hartree/Particle)
Thermal correction to Energy= 1.369629
Thermal correction to Enthalpy= 1.370573
Thermal correction to Gibbs Free Energy= 1.152514
Sum of electronic and zero-point Energies= -4472.172451
Sum of electronic and thermal Energies= -4472.082636
Sum of electronic and thermal Enthalpies= -4472.081691
Sum of electronic and thermal Free Energies= -4472.299751

Table S24. Atomic coordinates for the DFT optimized structure of (*S,S,P*)-**6:Ag**$_3$

	X	Y	Z				
C	-0.12281	-4.89183	-4.03354	C	-1.28571	-4.92671	2.311131
C	-0.40431	-4.6806	-2.69183	C	-1.67385	-5.17932	3.619384
C	-0.03086	-3.48725	-2.05679	C	-1.94091	-4.12144	4.48692
C	0.639033	-2.48545	-2.80512	C	-1.83266	-2.81327	4.038478
C	0.917695	-2.72303	-4.15914	C	-1.44598	-2.53679	2.720292
C	0.54254	-3.91197	-4.76765	C	-1.37063	-1.16959	2.325131
C	-0.35435	-3.35911	-0.67192	C	-1.38682	0.042922	2.155756
C	1.026948	-1.2202	-2.26788	C	1.406597	-0.09016	-1.97865
C	-0.73227	-3.41862	0.493974	C	1.809298	1.255637	-1.74359
C	-1.15575	-3.61128	1.842753	C	-1.3808	1.452682	1.976091
				C	-1.5835	2.025382	0.696068

C	-1.52551	3.40795	0.536286
C	-1.24917	4.231865	1.626142
C	-1.07651	3.676918	2.898862
C	-1.15149	2.302424	3.065747
C	2.074368	2.095413	-2.83828
C	2.43142	3.416378	-2.65279
C	2.510368	3.960004	-1.36276
C	2.261898	3.146256	-0.25659
C	1.94575	1.794483	-0.43939
O	2.892448	5.25286	-1.29608
O	-1.17372	5.556462	1.379473
C	-0.13993	6.302084	2.017698
C	2.523516	6.043029	-0.17353
C	1.060429	6.406294	-0.23732
C	0.543122	7.17203	0.984764
O	-0.35741	8.110512	0.445796
C	-0.30853	8.061435	-0.98124
O	0.853586	7.313188	-1.29436
C	-0.13452	9.458243	-1.52294
C	-1.55585	7.377159	-1.50882
H	-0.42201	-5.82418	-4.50663
H	-0.91613	-5.44416	-2.1094
H	1.437111	-1.95233	-4.72593
H	0.768814	-4.07316	-5.81915
H	-1.07468	-5.74858	1.629628
H	-1.76481	-6.20655	3.964387
H	-2.23653	-4.31704	5.515029
H	-2.03602	-1.97763	4.705427
H	-1.67853	3.851739	-0.44697
H	-0.90096	4.321869	3.756988
H	-1.03413	1.86905	4.057762
H	1.988992	1.689661	-3.84497
H	2.644155	4.064676	-3.49944
H	2.344769	3.524307	0.760959
H	-0.57168	6.922624	2.813046
H	0.598029	5.619544	2.47085
H	3.132778	6.950772	-0.24245
H	2.770038	5.541348	0.774174
H	0.465987	5.485973	-0.39102
H	1.375071	7.699078	1.488907
H	-0.05446	9.433477	-2.61588
H	-0.99632	10.07757	-1.24932
H	0.775496	9.904158	-1.10673
H	-1.51726	7.318318	-2.60357
H	-1.64784	6.365151	-1.09575
H	-2.44768	7.946029	-1.21813
C	-1.79986	1.220338	-0.46053
C	-1.99351	0.64268	-1.52125
C	-2.10748	0.001252	-2.78776
C	-2.70775	-1.27532	-2.9051
H	-3.19012	-2.89335	-4.23592
C	-2.7392	-1.90576	-4.15514
C	-2.19441	-1.28207	-5.26933
C	-1.62389	-0.01448	-5.15774
H	-1.20947	0.476856	-6.03494
C	-1.58081	0.624313	-3.92599
H	-1.13586	1.612929	-3.8265
C	1.885908	0.934531	0.696758
C	1.976344	0.180827	1.656419
C	2.038958	-0.7426	2.739623
C	1.677745	-0.35429	4.033799
H	1.392943	0.680555	4.215748
H	1.387688	-0.96934	6.069506
C	1.672257	-1.28144	5.06728
C	2.029838	-2.60687	4.82248
C	2.411677	-3.00603	3.548267
H	2.697954	-4.03769	3.35375
C	2.430474	-2.08526	2.494017
H	2.015341	-3.33377	5.631187
H	-2.22167	-1.78512	-6.23328
C	-3.25472	-1.94326	-1.77518
C	-3.74538	-2.57622	-0.85123
C	-4.26035	-3.50699	0.09486
C	-4.29091	-4.85794	-0.27646
H	-3.93735	-5.13329	-1.26833
C	-4.77105	-5.82235	0.59734
H	-4.79186	-6.86572	0.291472
C	-5.22495	-5.45208	1.861724
C	-5.20527	-4.11851	2.246565
H	-5.55928	-3.82233	3.232085
C	-4.73061	-3.12959	1.374654
C	-4.73379	-1.78009	1.833253
C	-4.77026	-0.67555	2.364101
C	-4.72535	0.484206	3.194781
C	-4.78238	1.807728	2.69538
C	-4.58531	0.27987	4.575572
H	-4.54549	-0.74108	4.951404
C	-4.49653	1.35496	5.447126
H	-4.38842	1.176065	6.514371
C	-4.54676	2.658231	4.954428
H	-4.47684	3.504071	5.634356
C	-4.6877	2.881013	3.593054
H	-4.71892	3.894678	3.19831
C	2.828812	-2.501	1.189022
C	3.205968	-2.86852	0.082648
C	3.559456	-3.46069	-1.16761

C	3.18501	-4.79395	-1.3838
H	2.638198	-5.31498	-0.59918
C	3.497938	-5.43736	-2.57183
H	3.191427	-6.46998	-2.72206
C	4.202138	-4.76138	-3.56618
C	4.583832	-3.44219	-3.37268
H	5.132918	-2.90868	-4.14565
C	4.270177	-2.7703	-2.18261
C	4.675558	-1.40558	-2.07397
C	5.062978	-0.24158	-2.13639
C	5.471718	1.10655	-2.36753
C	5.618495	2.063328	-1.33129
C	5.715175	1.493535	-3.69386
H	5.609591	0.75161	-4.4827
C	6.074934	2.798094	-3.99826
H	6.260488	3.077421	-5.03267
C	6.1908	3.745317	-2.98282
H	6.461239	4.771966	-3.21793
C	5.9647	3.379976	-1.6638
H	6.05567	4.113875	-0.86539
H	-5.6021	-6.20427	2.550788
H	4.453878	-5.26374	-4.4973
C	5.428507	1.753019	0.049791
C	5.322223	1.646217	1.266138
C	5.15471	1.544506	2.678752
C	4.725413	2.66317	3.402897
H	4.559216	3.601121	2.875123
C	4.515834	2.576507	4.772952
H	4.186947	3.454157	5.324764
C	4.725382	1.369232	5.43728
H	4.555006	1.29901	6.509209
C	5.152889	0.249104	4.735943
H	5.317219	-0.6965	5.248871
C	5.380633	0.31759	3.357966
C	5.803565	-0.83264	2.631838
C	6.160451	-1.79869	1.975785
C	6.510239	-2.90351	1.140465
C	7.292865	-2.69135	-0.00698
C	5.999751	-4.18352	1.405479
C	7.542343	-3.74136	-0.88017
C	6.253116	-5.22565	0.524299
C	7.01936	-5.00673	-0.61974
H	7.684171	-1.69405	-0.2075
H	5.393235	-4.34248	2.295714
H	5.846734	-6.21467	0.726771
H	7.20043	-5.82283	-1.3167
H	8.142434	-3.56978	-1.77147
C	-4.88614	2.111185	1.307091
C	-4.95065	2.540097	0.163579
C	-4.94101	3.08928	-1.1492
C	-4.47547	4.398149	-1.33832
H	-4.16888	4.980992	-0.4699
C	-4.40437	4.940645	-2.61403
H	-4.04267	5.958109	-2.74731
C	-4.79507	4.184453	-3.71807
H	-4.7362	4.608584	-4.71779
C	-5.26752	2.889825	-3.54871
H	-5.57932	2.298586	-4.40706
C	-5.35274	2.325572	-2.27071
C	-5.8337	0.994088	-2.10804
C	-6.28744	-0.13614	-2.00476
C	-6.77629	-1.47277	-1.89088
C	-7.38422	-1.90675	-0.70189
C	-6.59301	-2.37708	-2.94897
C	-7.77529	-3.23217	-0.56723
C	-6.99243	-3.69819	-2.80579
C	-7.57322	-4.12946	-1.61368
H	-7.54091	-1.19417	0.107734
H	-6.12768	-2.03122	-3.87075
H	-6.84715	-4.3984	-3.62592
H	-7.87416	-5.16931	-1.50145
H	-8.2335	-3.56914	0.360726
Ag	-4.36305	-0.09591	-0.12305
Ag	-0.05635	-0.96109	0.067561
Ag	4.427393	-0.59927	0.281539

Low frequencies --- -4.9730 -0.0097 -0.0066 -0.0061 6.8591 8.0253
Low frequencies --- 16.6950 18.6536 20.8474
Zero-point correction= 1.462252 (Hartree/Particle)
Thermal correction to Energy= 1.566540
Thermal correction to Enthalpy= 1.567485
Thermal correction to Gibbs Free Energy= 1.322770
Sum of electronic and zero-point Energies= -5231.606617
Sum of electronic and thermal Energies= -5231.502328

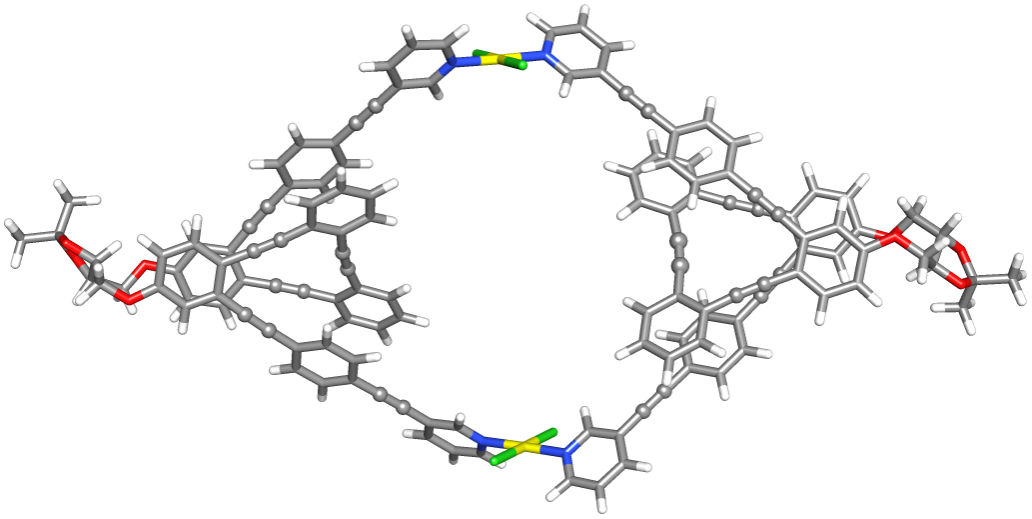
Sum of electronic and thermal Enthalpies= -5231.501384
Sum of electronic and thermal Free Energies= -5231.746099

Theoretical calculations of Pd(II) complexes

The optimization of the structure of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$ and its enantiomer ((*R*,*R*,*M*)-**7**)$_2$Pd$_2$ was carried out by means of DFT calculations with Gaussian 09,[12b] using the the ωB97XD density functional,[16] previously used in the optimization of this kind of structures.[17] The def2SVP basis set was used for C, H, N and O, while the LanL2DZ basis set and pseudopotential were used for Pd(II).[18] The calculations were carried out with an ultra-fine integration grid. The structures were optimized in two different solvents, DMSO and dichloromethane, applying the polarizable continuum model with the integral equation formalism (IEFPCM) available in Gaussian 09.[19] We checked the optimized structures corresponded to an energy minimum by frequency analysis.

The coordinates of the minimized structures are shown in Tables S22-S25.

Table S25. Atomic coordinates for the DFT optimized structure of ((*S*,*S*,*P*)-**7**)$_2$Pd$_2$ in CH_2Cl_2



Atom	X	Y	Z
C	14.355246	0.716747	-1.370255
C	13.922638	2.017637	-1.654705
H	14.632328	2.841461	-1.731123
C	11.617563	1.236891	-1.761556
C	12.067692	-0.080638	-1.490175
C	12.566973	2.262686	-1.844914
C	13.428255	-0.325388	-1.301286
H	13.780874	-1.331037	-1.070705
C	10.225820	1.525142	-1.912478
C	9.047176	1.801053	-2.009110
C	7.676719	2.186993	-2.142157
C	7.339114	3.229427	-3.022119
H	8.135438	3.715336	-3.588324
C	6.021583	3.643324	-3.170161
H	5.782226	4.460227	-3.853504
C	5.009476	3.018595	-2.439512
H	3.972646	3.342520	-2.547271
C	5.323877	1.987216	-1.563954
H	4.538309	1.501528	-0.982509
C	6.652326	1.558520	-1.395554
C	6.909388	0.514621	-0.448353
C	6.978486	-0.361484	0.391680
C	6.880480	-1.425724	1.345920
C	5.638522	-2.071123	1.485500
H	4.803038	-1.737455	0.867746
C	5.470843	-3.120435	2.379232
H	4.499885	-3.611776	2.464162
C	6.548134	-3.548151	3.157098
H	6.426585	-4.376319	3.857901
C	7.781044	-2.920341	3.036863
H	8.627354	-3.251310	3.641202
C	7.970571	-1.855535	2.138428
C	9.265471	-1.251415	2.052783
C	10.395340	-0.805377	2.037509
C	11.740444	-0.318542	2.056840
C	12.035510	1.052624	1.842590
C	13.356618	1.498183	1.913308
H	13.589125	2.552064	1.757640
C	14.400237	0.612010	2.197906
C	14.120332	-0.747509	2.379469
H	14.910090	-1.470083	2.582916
C	12.803807	-1.193182	2.310133
O	15.629385	1.168769	2.292293
O	15.641563	0.383264	-1.148486
C	11.125922	-1.147849	-1.366657
H	12.230314	3.278775	-2.057347
H	12.591891	-2.252764	2.462655

C	10.981209	1.973498	1.552627
C	10.297474	-2.021521	-1.218033
C	10.064618	2.719986	1.278974
C	9.296592	-3.006208	-0.950177
C	8.027215	-2.914208	-1.544326
C	9.554271	-4.038789	-0.033152
C	7.027970	-3.814090	-1.203320
H	7.823208	-2.111779	-2.254305
C	8.555032	-4.935791	0.310658
H	10.538842	-4.110399	0.431472
C	7.276065	-4.825687	-0.260988
H	6.036695	-3.725588	-1.650623
H	8.752053	-5.721347	1.041792
C	8.981033	3.567682	0.888085
C	9.206195	4.636013	0.002976
C	7.676831	3.314113	1.341521
C	8.148480	5.415388	-0.437565
H	10.218386	4.833813	-0.353033
C	6.617556	4.097344	0.903628
H	7.497323	2.481100	2.022317
C	6.839595	5.150246	0.002314
H	8.325394	6.233143	-1.138042
H	5.603514	3.885514	1.245964
C	6.236510	-5.725948	0.134687
C	5.362603	-6.488743	0.492325
C	5.750493	5.944362	-0.479032
C	4.841971	6.628616	-0.902942
C	4.347806	-7.398917	0.923286
C	3.090028	-7.397124	0.307958
C	4.575964	-8.320718	1.956205
H	2.870421	-6.721712	-0.518789
C	3.555080	-9.184918	2.328015
H	5.546293	-8.352198	2.454151
C	2.333344	-9.113373	1.671948
H	3.694993	-9.915334	3.124763
H	1.495015	-9.753293	1.946330
C	3.793874	7.459159	-1.409007
C	2.530004	7.449971	-0.806559
C	3.998908	8.316968	-2.500201
H	2.326227	6.824597	0.062604
C	2.950930	9.115401	-2.937450
H	4.973014	8.351957	-2.990502
C	1.726598	9.044593	-2.286106
H	3.072137	9.795670	-3.780339
H	0.870149	9.636562	-2.607729
N	1.531541	8.226262	-1.240586
N	2.117490	-8.234777	0.681068
Pd	-0.294820	8.209714	-0.279917

Pd	0.294851	-8.209482	-0.280353
N	-2.117654	8.234881	0.681139
C	-3.090101	7.397226	0.307793
C	-2.333695	9.113373	1.672069
C	-4.347967	7.398899	0.922943
H	-2.870337	6.721910	-0.518991
C	-3.555532	9.184806	2.327958
H	-1.495433	9.753298	1.946643
C	-5.362673	6.488711	0.491799
C	-4.576318	8.320592	1.955917
H	-3.695596	9.915141	3.124755
C	-6.236551	5.725910	0.134101
H	-5.546720	8.351974	2.453725
C	-7.276110	4.825653	-0.261570
C	-7.028066	3.814086	-1.203946
C	-8.555042	4.935729	0.310162
C	-8.027324	2.914201	-1.544909
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C	-9.554293	4.038725	-0.033605
H	-8.752023	5.721263	1.041330
C	-9.296662	3.006168	-0.950671
H	-7.823355	2.111792	-2.254921
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C	-10.297555	2.021476	-1.218465
C	-11.126048	1.147827	-1.366976
C	-12.067788	0.080583	-1.490438
C	-11.617626	-1.236922	-1.761886
C	-13.428346	0.325271	-1.301430
C	-12.567002	-2.262752	-1.845192
C	-10.225883	-1.525111	-1.912919
C	-14.355300	-0.716901	-1.370343
H	-13.780988	1.330901	-1.070798
C	-13.922660	-2.017765	-1.654864
H	-12.230317	-3.278822	-2.057678
C	-9.047235	-1.800969	-2.009643
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C	-7.676770	-2.186845	-2.142786
C	-7.339170	-3.229221	-3.022819
C	-6.652362	-1.558370	-1.396205
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C	-6.021630	-3.643059	-3.170950
C	-5.323906	-1.987007	-1.564693
C	-6.909416	-0.514525	-0.448941
H	-5.782277	-4.459919	-3.854347
C	-5.009510	-3.018330	-2.440319
H	-4.538327	-1.501318	-0.983265
C	-6.978511	0.361543	0.391130

H	-3.972674	-3.342211	-2.548147
C	-6.880512	1.425760	1.345396
O	-15.629270	-1.169106	2.292264
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C	-7.970586	1.855494	2.137970
C	-14.400148	-0.612301	2.197806
H	-4.803108	1.737608	0.867131
C	-5.470906	3.120507	2.378695
C	-7.781065	2.920281	3.036430
C	-9.265462	1.251319	2.052372
C	-13.356519	-1.498429	1.913102
C	-14.120277	0.747221	2.379390
H	-4.499967	3.611893	2.463592
C	-6.548180	3.548146	3.156627
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C	-10.064530	-2.720097	1.278458
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H	-8.325328	-6.233063	-1.138859
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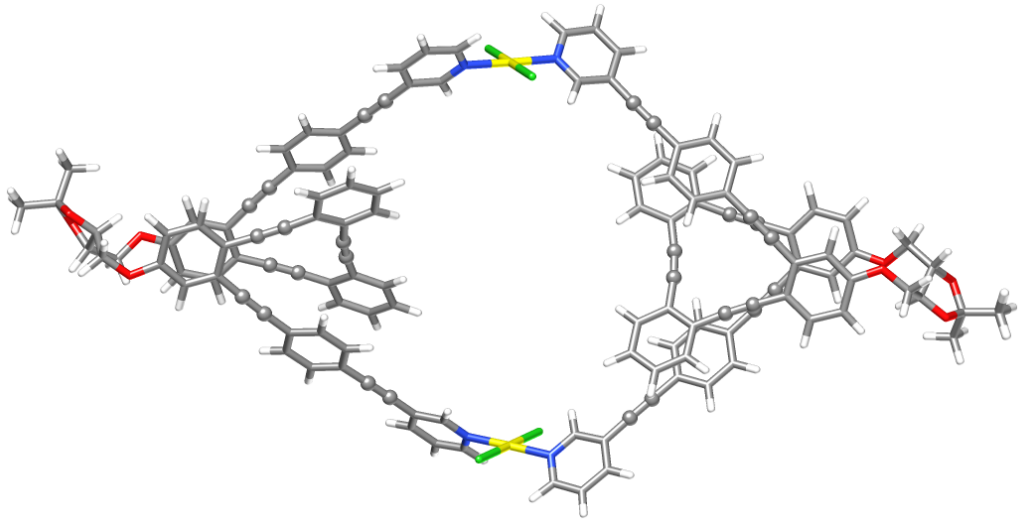
Cl	-0.799973	-8.237751	1.809791
C	16.779726	0.366057	2.466038
C	17.193795	-0.250500	1.142575
H	16.623172	-0.414644	3.226880
H	17.566255	1.038882	2.833492
C	17.659226	0.739433	0.073977
H	16.357276	-0.846143	0.734899
O	18.337148	-1.047424	1.316650
C	16.557816	1.377443	-0.743147
H	18.236127	1.558685	0.547586
O	18.504505	-0.060033	-0.719353
C	18.974631	-1.161494	0.052351
H	16.055906	2.124180	-0.107045
H	16.989284	1.892028	-1.617708
C	18.556915	-2.447385	-0.645858
C	20.472975	-1.051227	0.265999
H	18.893321	-3.321324	-0.070995
H	18.999084	-2.491321	-1.650822
H	17.463043	-2.480410	-0.747920
H	20.707101	-0.090335	0.744690
H	20.998050	-1.110815	-0.697079
H	20.826291	-1.866586	0.912577
C	-16.557803	-1.377716	-0.743126
H	-16.055839	-2.124458	-0.107073
H	-16.989277	-1.892282	-1.617696
C	-17.659217	-0.739792	0.074061
H	-18.236054	-1.559092	0.547667
C	-17.193800	0.250135	1.142669
H	-16.357344	0.845847	0.734966
C	-16.779629	-0.366439	2.466093
H	-16.623062	0.414248	3.226946
H	-17.566114	-1.039302	2.833573
C	-18.974768	1.161031	0.052569
C	-18.557225	2.446995	-0.645608
H	-18.893691	3.320874	-0.070689
H	-18.999453	2.490928	-1.650546
H	-17.463361	2.480139	-0.747725
C	-20.473088	1.050598	0.266300
H	-20.707087	0.089659	0.744959
H	-20.998227	1.110179	-0.696743
H	-20.826450	1.865888	0.912940
O	-18.504569	0.059654	-0.719210
O	-18.337200	1.046975	1.316828

Charge = 0; multiplicity = 0; (0 imaginary frequencies)

Zero-point correction = 1.813554 (Hartree/Particle)
Thermal correction to Energy = 1.944357
Thermal correction to Enthalpy = 1.945302
Thermal correction to Gibbs Free Energy = 1.623814
Sum of electronic and zero-point Energies = –8062.833420
Sum of electronic and thermal Energies = –8062.702617
Sum of electronic and thermal Enthalpies = –8062.701673
Sum of electronic and thermal Free Energies = –8063.023160

Table S26. Atomic coordinates for the DFT optimized structure of ((*S,S,P*)-**7**)$_2$Pd$_2$ in DMSO



Atom	X	Y	Z
C	-14.292588	-0.725860	-1.373834
C	-13.863697	-2.031881	-1.640717
H	-14.575334	-2.855060	-1.704227
C	-11.556844	-1.258626	-1.760100
C	-12.003139	0.063782	-1.507030
C	-12.508961	-2.283354	-1.828521
C	-13.362817	0.315046	-1.320260
H	-13.712719	1.324528	-1.102337
C	-10.165630	-1.553342	-1.905628
C	-8.988064	-1.837233	-1.996253
C	-7.620263	-2.236240	-2.122577
C	-7.290704	-3.291615	-2.990033
H	-8.089930	-3.778385	-3.551348
C	-5.976263	-3.718103	-3.131162
H	-5.743146	-4.545250	-3.804184
C	-4.959932	-3.093522	-2.406205
H	-3.925768	-3.427419	-2.508829
C	-5.266448	-2.049727	-1.542389
H	-4.477395	-1.564465	-0.965362
C	-6.591538	-1.608225	-1.381321
C	-6.841610	-0.550269	-0.447508
C	-6.906011	0.339337	0.379074
C	-6.804583	1.418540	1.316335
C	-5.559827	2.059667	1.449583

H	-4.722928	1.710934	0.842162
C	-5.391750	3.124610	2.324856
H	-4.418839	3.612742	2.405772
C	-6.470844	3.572708	3.088753
H	-6.349044	4.414360	3.773151
C	-7.706532	2.948956	2.974581
H	-8.553986	3.296616	3.567770
C	-7.896102	1.867561	2.096223
C	-9.192138	1.264100	2.018587
C	-10.322687	0.818641	2.011759
C	-11.669549	0.336405	2.038719
C	-11.969702	-1.036372	1.842416
C	-13.292422	-1.476012	1.917494
H	-13.529419	-2.530697	1.774241
C	-14.332842	-0.581857	2.190214
C	-14.047645	0.778856	2.355201
H	-14.834619	1.507034	2.549136
C	-12.729532	1.218718	2.280568
O	-15.563119	-1.132878	2.290192
O	-15.577077	-0.385434	-1.155783
C	-11.059392	1.131154	-1.396485
H	-12.175819	-3.303511	-2.026410
H	-12.514060	2.279481	2.419289
C	-10.919601	-1.966560	1.565246
C	-10.234991	2.010035	-1.253654
C	-10.010520	-2.725913	1.300877
C	-9.242286	3.003349	-0.985454
C	-7.964164	2.910750	-1.560301
C	-9.518770	4.045140	-0.084153
C	-6.974245	3.819731	-1.215525
H	-7.745039	2.101820	-2.258466
C	-8.529239	4.951619	0.262781
H	-10.510070	4.117654	0.365863
C	-7.241564	4.841349	-0.289479
H	-5.976175	3.730606	-1.647289
H	-8.741035	5.744643	0.981584
C	-8.936925	-3.589368	0.915521
C	-9.175766	-4.659079	0.035516
C	-7.629398	-3.349050	1.366883
C	-8.127527	-5.452806	-0.402363
H	-10.190233	-4.847118	-0.319277
C	-6.579546	-4.146159	0.931172
H	-7.438306	-2.516171	2.044897
C	-6.815131	-5.200421	0.034803
H	-8.314971	-6.271116	-1.099374
H	-5.562823	-3.944097	1.271470
C	-6.213148	5.753187	0.109186
C	-5.350668	6.527607	0.469511

C	-5.735538	-6.008654	-0.444617
C	-4.835137	-6.704349	-0.867192
C	-4.351328	7.453807	0.902920
C	-3.086301	7.459310	0.303146
C	-4.603391	8.385145	1.921807
H	-2.847433	6.773753	-0.509838
C	-3.597898	9.267009	2.294294
H	-5.579567	8.410709	2.408385
C	-2.368165	9.203620	1.652380
H	-3.756584	10.005636	3.079777
H	-1.543489	9.861371	1.925763
C	-3.796886	-7.549267	-1.370057
C	-2.526260	-7.534002	-0.782574
C	-4.018869	-8.427437	-2.441720
H	-2.308779	-6.890568	0.069890
C	-2.979909	-9.240206	-2.874434
H	-4.998338	-8.467195	-2.920702
C	-1.748222	-9.163414	-2.237764
H	-3.114416	-9.936621	-3.701897
H	-0.898972	-9.767830	-2.555483
N	-1.537147	-8.324775	-1.211527
N	-2.129308	8.314820	0.676034
Pd	0.297621	-8.300014	-0.268804
Pd	-0.297660	8.300018	-0.266704
N	2.129244	-8.314951	0.673971
C	3.086246	-7.459384	0.301237
C	2.368070	-9.203895	1.650193
C	4.351252	-7.453965	0.901059
H	2.847401	-6.773711	-0.511657
C	3.597783	-9.267381	2.292135
H	1.543386	-9.861688	1.923453
C	5.350604	-6.527684	0.467852
C	4.603284	-8.385457	1.919814
H	3.756446	-10.006126	3.077512
C	6.213103	-5.753188	0.107738
H	5.579444	-8.411089	2.406420
C	7.241550	-4.841259	-0.290641
C	6.974291	-3.819382	-1.216420
C	8.529195	-4.951696	0.261654
C	7.964237	-2.910313	-1.560887
H	5.976246	-3.730128	-1.648215
C	9.518753	-4.045129	-0.084972
H	8.740945	-5.744922	0.980247
C	9.242326	-3.003081	-0.985994
H	7.745159	-2.101190	-2.258842
H	10.510028	-4.117779	0.365076
C	10.235053	-2.009699	-1.253861
C	11.059494	-1.130807	-1.396391

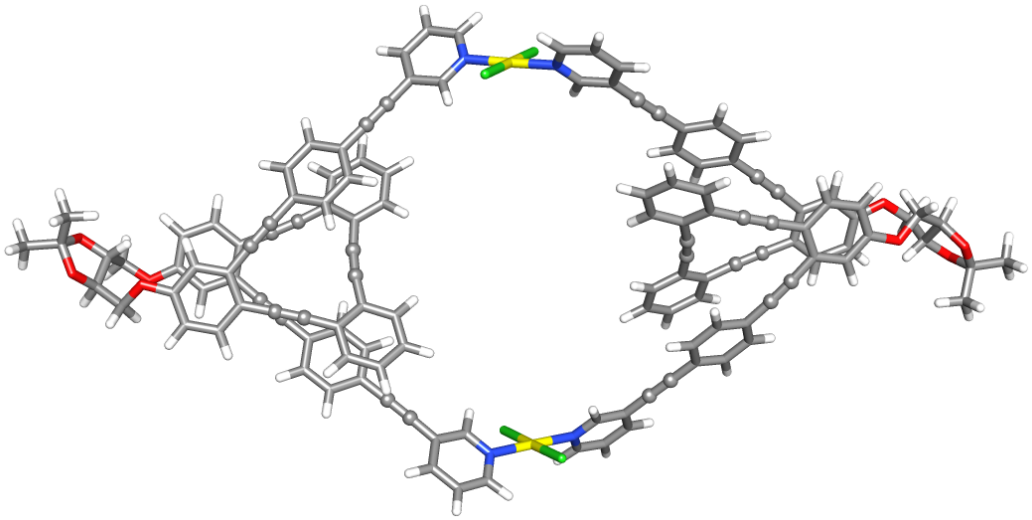
C	12.003208	-0.063373	-1.506617
C	11.556867	1.259082	-1.759360
C	13.362888	-0.314628	-1.319854
C	12.508942	2.283869	-1.827470
C	10.165646	1.553782	-1.904858
C	14.292616	0.726334	-1.373112
H	13.712824	-1.324151	-1.102178
C	13.863679	2.032406	-1.639668
H	12.175764	3.304063	-2.025105
C	8.988073	1.837664	-1.995426
O	15.577111	0.385912	-1.155092
H	14.575284	2.855632	-1.702924
C	7.620270	2.236694	-2.121657
C	7.290708	3.292272	-2.988865
C	6.591547	1.608507	-1.380545
H	8.089933	3.779174	-3.550068
C	5.976268	3.718796	-3.129888
C	5.266456	2.050048	-1.541504
C	6.841620	0.550322	-0.446991
H	5.743149	4.546102	-3.802714
C	4.959938	3.094046	-2.405074
H	4.477405	1.564651	-0.964589
C	6.906022	-0.339506	0.379351
H	3.925775	3.427969	-2.507616
C	6.804618	-1.418978	1.316303
O	15.563095	1.132346	2.291104
C	5.559886	-2.060194	1.449344
C	7.896145	-1.868184	2.096074
C	14.332830	0.581337	2.190916
H	4.722982	-1.711317	0.842012
C	5.391839	-3.125402	2.324300
C	7.706606	-2.949846	2.974109
C	9.192157	-1.264649	2.018633
C	13.292413	1.475553	1.918384
C	14.047639	-0.779423	2.355532
H	4.418947	-3.613598	2.405058
C	6.470942	-3.573682	3.088078
H	8.554065	-3.297648	3.567207
C	10.322694	-0.819153	2.011954
C	11.969699	1.035922	1.843139
H	13.529405	2.530278	1.775417
H	14.834611	-1.507645	2.549307
C	12.729532	-1.219276	2.280734
H	6.349166	-4.415542	3.772225
C	11.669550	-0.336907	2.039078
C	10.919603	1.966172	1.566164
H	12.514063	-2.280076	2.419170
C	10.010531	2.725590	1.301949

C	8.936931	3.589122	0.916782
C	9.175759	4.659027	0.037010
C	7.629407	3.348695	1.368098
C	8.127510	5.452841	-0.400689
H	10.190221	4.847154	-0.317745
C	6.579547	4.145891	0.932570
H	7.438326	2.515668	2.045934
C	6.815119	5.200350	0.036429
H	8.314944	6.271305	-1.097524
H	5.562828	3.943747	1.272829
C	5.735517	6.008671	-0.442821
C	4.835112	6.704440	-0.865266
C	3.796864	7.549437	-1.368003
C	2.526234	7.534087	-0.780532
C	4.018856	8.427763	-2.439537
H	2.308745	6.890532	0.071838
N	1.537123	8.324916	-1.209388
C	2.979899	9.240591	-2.872147
H	4.998330	8.467590	-2.918503
C	1.748205	9.163700	-2.235503
H	3.114414	9.937124	-3.699509
H	0.898954	9.768154	-2.553148
Cl	1.386466	-8.268570	-2.364701
Cl	-0.778393	-8.317509	1.834435
Cl	-1.386438	8.268707	-2.362640
Cl	0.778327	8.317391	1.836547
C	-16.711860	-0.325958	2.459826
C	-17.128598	0.280327	1.132410
H	-16.551214	0.460405	3.213811
H	-17.498682	-0.994449	2.834218
C	-17.595262	-0.716593	0.071615
H	-16.294822	0.875781	0.718693
O	-18.273754	1.075914	1.304754
C	-16.498031	-1.371030	-0.737044
H	-18.181481	-1.526169	0.550023
O	-18.428177	0.086224	-0.732441
C	-18.930584	1.167233	0.047109
H	-15.999754	-2.112148	-0.091963
H	-16.931626	-1.894769	-1.604885
C	-18.567995	2.468415	-0.652175
C	-20.421654	1.002051	0.278863
H	-18.933964	3.327714	-0.073422
H	-19.019381	2.497668	-1.653666
H	-17.476683	2.543931	-0.759653
H	-20.616409	0.029852	0.752588
H	-20.961449	1.051347	-0.676687
H	-20.795083	1.799258	0.936707
C	16.497983	1.371444	-0.736021

H	15.999636	2.112312	-0.090706
H	16.931554	1.895496	-1.603684
C	17.595250	0.716833	0.072449
H	18.181395	1.526304	0.551125
C	17.128637	-0.280453	1.132924
H	16.294903	-0.875831	0.719017
C	16.711850	0.325399	2.460521
H	16.551207	-0.461202	3.214258
H	17.498646	0.993793	2.835140
C	18.930643	-1.166943	0.047341
C	18.568015	-2.467888	-0.652367
H	18.933980	-3.327386	-0.073907
H	19.019379	-2.496815	-1.653877
H	17.476699	-2.543350	-0.759850
C	20.421721	-1.001870	0.279119
H	20.616504	-0.029835	0.753169
H	20.961494	-1.050853	-0.676460
H	20.795148	-1.799308	0.936684
O	18.428248	-0.085663	-0.731843
O	18.273841	-1.076023	1.305026

Charge = 0; multiplicity = 0; (0 imaginary frequencies)
Zero-point correction = 1.813059 (Hartree/Particle)
Thermal correction to Energy = 1.944009
Thermal correction to Enthalpy = 1.944953
Thermal correction to Gibbs Free Energy = 1.623093
Sum of electronic and zero-point Energies = –8062.847995
Sum of electronic and thermal Energies = –8062.717045
Sum of electronic and thermal Enthalpies = –8062.716101
Sum of electronic and thermal Free Energies = –8063.037961

Table S27. Atomic coordinates for the DFT optimized structure of ((*R,R,M*)-**7**)$_2$Pd$_2$ in CH_2Cl_2



Atom	X	Y	Z
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C	13.922638	2.017637	1.654705
H	14.632328	2.841461	1.731123
C	11.617563	1.236891	1.761556
C	12.067692	-0.080638	1.490175
C	12.566973	2.262686	1.844914
C	13.428255	-0.325388	1.301286
H	13.780874	-1.331037	1.070705
C	10.225820	1.525142	1.912478
C	9.047176	1.801053	2.009110
C	7.676719	2.186993	2.142157
C	7.339114	3.229427	3.022119
H	8.135438	3.715336	3.588324
C	6.021583	3.643324	3.170161
H	5.782226	4.460227	3.853504
C	5.009476	3.018595	2.439512
H	3.972646	3.342520	2.547271
C	5.323877	1.987216	1.563954
H	4.538309	1.501528	0.982509
C	6.652326	1.558520	1.395554
C	6.909388	0.514621	0.448353
C	6.978486	-0.361484	-0.391680
C	6.880480	-1.425724	-1.345920
C	5.638522	-2.071123	-1.485500
H	4.803038	-1.737455	-0.867746
C	5.470843	-3.120435	-2.379232
H	4.499885	-3.611776	-2.464162
C	6.548134	-3.548151	-3.157098
H	6.426585	-4.376319	-3.857901
C	7.781044	-2.920341	-3.036863
H	8.627354	-3.251310	-3.641202
C	7.970571	-1.855535	-2.138428
C	9.265471	-1.251415	-2.052783
C	10.395340	-0.805377	-2.037509
C	11.740444	-0.318542	-2.056840
C	12.035510	1.052624	-1.842590
C	13.356618	1.498183	-1.913308
H	13.589125	2.552064	-1.757640
C	14.400237	0.612010	-2.197906
C	14.120332	-0.747509	-2.379469
H	14.910090	-1.470083	-2.582916
C	12.803807	-1.193182	-2.310133
O	15.629385	1.168769	-2.292293
O	15.641563	0.383264	1.148486
C	11.125922	-1.147849	1.366657
H	12.230314	3.278775	2.057347
H	12.591891	-2.252764	-2.462655
C	10.981209	1.973498	-1.552627
C	10.297474	-2.021521	1.218033

C	10.064618	2.719986	-1.278974
C	9.296592	-3.006208	0.950177
C	8.027215	-2.914208	1.544326
C	9.554271	-4.038789	0.033152
C	7.027970	-3.814090	1.203320
H	7.823208	-2.111779	2.254305
C	8.555032	-4.935791	-0.310658
H	10.538842	-4.110399	-0.431472
C	7.276065	-4.825687	0.260988
H	6.036695	-3.725588	1.650623
H	8.752053	-5.721347	-1.041792
C	8.981033	3.567682	-0.888085
C	9.206195	4.636013	-0.002976
C	7.676831	3.314113	-1.341521
C	8.148480	5.415388	0.437565
H	10.218386	4.833813	0.353033
C	6.617556	4.097344	-0.903628
H	7.497323	2.481100	-2.022317
C	6.839595	5.150246	-0.002314
H	8.325394	6.233143	1.138042
H	5.603514	3.885514	-1.245964
C	6.236510	-5.725948	-0.134687
C	5.362603	-6.488743	-0.492325
C	5.750493	5.944362	0.479032
C	4.841971	6.628616	0.902942
C	4.347806	-7.398917	-0.923286
C	3.090028	-7.397124	-0.307958
C	4.575964	-8.320718	-1.956205
H	2.870421	-6.721712	0.518789
C	3.555080	-9.184918	-2.328015
H	5.546293	-8.352198	-2.454151
C	2.333344	-9.113373	-1.671948
H	3.694993	-9.915334	-3.124763
H	1.495015	-9.753293	-1.946330
C	3.793874	7.459159	1.409007
C	2.530004	7.449971	0.806559
C	3.998908	8.316968	2.500201
H	2.326227	6.824597	-0.062604
C	2.950930	9.115401	2.937450
H	4.973014	8.351957	2.990502
C	1.726598	9.044593	2.286106
H	3.072137	9.795670	3.780339
H	0.870149	9.636562	2.607729
N	1.531541	8.226262	1.240586
N	2.117490	-8.234777	-0.681068
Pd	-0.294820	8.209714	0.279917
Pd	0.294851	-8.209482	0.280353
N	-2.117654	8.234881	-0.681139

C	-3.090101	7.397226	-0.307793
C	-2.333695	9.113373	-1.672069
C	-4.347967	7.398899	-0.922943
H	-2.870337	6.721910	0.518991
C	-3.555532	9.184806	-2.327958
H	-1.495433	9.753298	-1.946643
C	-5.362673	6.488711	-0.491799
C	-4.576318	8.320592	-1.955917
H	-3.695596	9.915141	-3.124755
C	-6.236551	5.725910	-0.134101
H	-5.546720	8.351974	-2.453725
C	-7.276110	4.825653	0.261570
C	-7.028066	3.814086	1.203946
C	-8.555042	4.935729	-0.310162
C	-8.027324	2.914201	1.544909
H	-6.036819	3.725605	1.651316
C	-9.554293	4.038725	0.033605
H	-8.752023	5.721263	-1.041330
C	-9.296662	3.006168	0.950671
H	-7.823355	2.111792	2.254921
H	-10.538834	4.110310	-0.431089
C	-10.297555	2.021476	1.218465
C	-11.126048	1.147827	1.366976
C	-12.067788	0.080583	1.490438
C	-11.617626	-1.236922	1.761886
C	-13.428346	0.325271	1.301430
C	-12.567002	-2.262752	1.845192
C	-10.225883	-1.525111	1.912919
C	-14.355300	-0.716901	1.370343
H	-13.780988	1.330901	1.070798
C	-13.922660	-2.017765	1.654864
H	-12.230317	-3.278822	2.057678
C	-9.047235	-1.800969	2.009643
O	-15.641610	-0.383476	1.148450
H	-14.632321	-2.841619	1.731241
C	-7.676770	-2.186845	2.142786
C	-7.339170	-3.229221	3.022819
C	-6.652362	-1.558370	1.396205
H	-8.135505	-3.715132	3.589008
C	-6.021630	-3.643059	3.170950
C	-5.323906	-1.987007	1.564693
C	-6.909416	-0.514525	0.448941
H	-5.782277	-4.459919	3.854347
C	-5.009510	-3.018330	2.440319
H	-4.538327	-1.501318	0.983265
C	-6.978511	0.361543	-0.391130
H	-3.972674	-3.342211	2.548147
C	-6.880512	1.425760	-1.345396

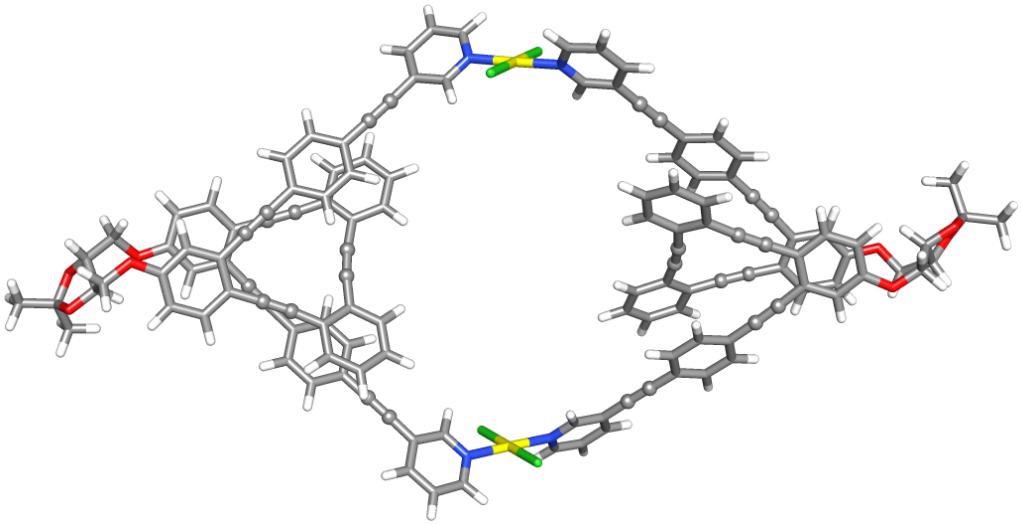
O	-15.629270	-1.169106	-2.292264
C	-5.638578	2.071216	-1.484937
C	-7.970586	1.855494	-2.137970
C	-14.400148	-0.612301	-2.197806
H	-4.803108	1.737608	-0.867131
C	-5.470906	3.120507	-2.378695
C	-7.781065	2.920281	-3.036430
C	-9.265462	1.251319	-2.052372
C	-13.356519	-1.498429	-1.913102
C	-14.120277	0.747221	-2.379390
H	-4.499967	3.611893	-2.463592
C	-6.548180	3.548146	-3.156627
H	-8.627362	3.251189	-3.640821
C	-10.395313	0.805233	-2.037158
C	-12.035432	-1.052822	-1.842297
H	-13.589002	-2.552313	-1.757417
H	-14.910045	1.469762	-2.582919
C	-12.803772	1.192942	-2.309972
H	-6.426636	4.376296	-3.857452
C	-11.740398	0.318347	-2.056571
C	-10.981123	-1.973650	-1.552215
H	-12.591881	2.252526	-2.462512
C	-10.064530	-2.720097	-1.278458
C	-8.980941	-3.567735	-0.887452
C	-9.206118	-4.636030	-0.002303
C	-7.676719	-3.314136	-1.340814
C	-8.148400	-5.415338	0.438351
H	-10.218325	-4.833854	0.353645
C	-6.617442	-4.097301	-0.902810
H	-7.497199	-2.481150	-2.021639
C	-6.839497	-5.150165	-0.001453
H	-8.325328	-6.233063	1.138859
H	-5.603385	-3.885447	-1.245089
C	-5.750383	-5.944200	0.479999
C	-4.841827	-6.628367	0.903976
C	-3.793642	-7.458788	1.410059
C	-2.529871	-7.449684	0.807400
C	-3.998473	-8.316392	2.501450
H	-2.326258	-6.824468	-0.061914
N	-1.531317	-8.225875	1.241399
C	-2.950401	-9.114714	2.938676
H	-4.972496	-8.351313	2.991922
C	-1.726180	-9.044009	2.287110
H	-3.071448	-9.794823	3.781717
H	-0.869665	-9.635902	2.608699
Cl	-1.402286	8.163181	2.362893
Cl	0.799597	8.237769	-1.810443
Cl	1.402748	-8.162743	2.363100

Cl	-0.799973	-8.237751	-1.809791
C	16.779726	0.366057	-2.466038
C	17.193795	-0.250500	-1.142575
H	16.623172	-0.414644	-3.226880
H	17.566255	1.038882	-2.833492
C	17.659226	0.739433	-0.073977
H	16.357276	-0.846143	-0.734899
O	18.337148	-1.047424	-1.316650
C	16.557816	1.377443	0.743147
H	18.236127	1.558685	-0.547586
O	18.504505	-0.060033	0.719353
C	18.974631	-1.161494	-0.052351
H	16.055906	2.124180	0.107045
H	16.989284	1.892028	1.617708
C	18.556915	-2.447385	0.645858
C	20.472975	-1.051227	-0.265999
H	18.893321	-3.321324	0.070995
H	18.999084	-2.491321	1.650822
H	17.463043	-2.480410	0.747920
H	20.707101	-0.090335	-0.744690
H	20.998050	-1.110815	0.697079
H	20.826291	-1.866586	-0.912577
C	-16.557803	-1.377716	0.743126
H	-16.055839	-2.124458	0.107073
H	-16.989277	-1.892282	1.617696
C	-17.659217	-0.739792	-0.074061
H	-18.236054	-1.559092	-0.547667
C	-17.193800	0.250135	-1.142669
H	-16.357344	0.845847	-0.734966
C	-16.779629	-0.366439	-2.466093
H	-16.623062	0.414248	-3.226946
H	-17.566114	-1.039302	-2.833573
C	-18.974768	1.161031	-0.052569
C	-18.557225	2.446995	0.645608
H	-18.893691	3.320874	0.070689
H	-18.999453	2.490928	1.650546
H	-17.463361	2.480139	0.747725
C	-20.473088	1.050598	-0.266300
H	-20.707087	0.089659	-0.744959
H	-20.998227	1.110179	0.696743
H	-20.826450	1.865888	-0.912940
O	-18.504569	0.059654	0.719210
O	-18.337200	1.046975	-1.316828

Charge = 0; multiplicity = 0; (0 imaginary frequencies)
Zero-point correction = 1.813554 (Hartree/Particle)
Thermal correction to Energy = 1.944357
Thermal correction to Enthalpy = 1.945302

Thermal correction to Gibbs Free Energy = 1.623814
Sum of electronic and zero-point Energies = –8062.833420
Sum of electronic and thermal Energies = –8062.702617
Sum of electronic and thermal Enthalpies = –8062.701673
Sum of electronic and thermal Free Energies = –8063.023160

Table S28. Atomic coordinates for the DFT optimized structure of ((*R,R,M*)-**7**)$_2$Pd$_2$ in DMSO



Atom	X	Y	Z
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C	-13.8637615	2.0311231	-1.6405741
H	-14.5754409	2.8542657	-1.7040831
C	-11.5568700	1.2579848	-1.7599582
C	-12.0030979	-0.0644459	-1.5068915
C	-12.5090389	2.2826644	-1.8283783
C	-13.3627625	-0.3157792	-1.3201221
H	-13.7126138	-1.3252794	-1.1022004
C	-10.1656706	1.5527717	-1.9054856
C	-8.9881192	1.8367230	-1.9961095
C	-7.6203383	2.2357998	-2.1224329
C	-7.2908327	3.2911930	-2.9898869
H	-8.0900832	3.7779236	-3.5512012
C	-5.9764136	3.7177483	-3.1310139
H	-5.7433380	4.5449090	-3.8040347
C	-4.9600507	3.0932180	-2.4060572
H	-3.9259038	3.4271681	-2.5086807
C	-5.2665136	2.0494055	-1.5422434
H	-4.4774363	1.5641829	-0.9652170
C	-6.5915819	1.6078362	-1.3811776
C	-6.8416005	0.5498652	-0.4473663
C	-6.9059559	-0.3397456	0.3792138
C	-6.8044740	-1.4189449	1.3164723
C	-5.5596854	-2.0600093	1.4497201
H	-4.7228040	-1.7112331	0.8423000
C	-5.3915548	-3.1249456	2.3249910

H	-4.4186188	-3.6130284	2.4059059
C	-6.4706266	-3.5730999	3.0888862
H	-6.3487838	-4.4147477	3.7732820
C	-7.7063456	-2.9494106	2.9747152
H	-8.5537826	-3.2971151	3.5679029
C	-7.8959707	-1.8680234	2.0963591
C	-9.1920363	-1.2646277	2.0187245
C	-10.3226088	-0.8192263	2.0118968
C	-11.6694951	-0.3370586	2.0388570
C	-11.9697178	1.0357036	1.8425570
C	-13.2924602	1.4752753	1.9176352
H	-13.5295107	2.5299487	1.7743846
C	-14.3328348	0.5810673	2.1903540
C	-14.0475687	-0.7796316	2.3553385
H	-14.8345053	-1.5078503	2.5492720
C	-12.7294331	-1.2194265	2.2807047
O	-15.5631396	1.1320254	2.2903332
O	-15.5770582	0.3845881	-1.1556439
C	-11.0592970	-1.1317705	-1.3963477
H	-12.1759480	3.3028388	-2.0262651
H	-12.5139071	-2.2801785	2.4194230
C	-10.9196645	1.9659450	1.5653891
C	-10.2348515	-2.0106101	-1.2535183
C	-10.0106220	2.7253451	1.3010214
C	-9.2420961	-3.0038741	-0.9853201
C	-7.9639786	-2.9112098	-1.5601666
C	-9.5185280	-4.0456817	-0.0840219
C	-6.9740135	-3.8201417	-1.2153916
H	-7.7448943	-2.1022671	-2.2583291
C	-8.5289517	-4.9521109	0.2629109
H	-10.5098246	-4.1182462	0.3659942
C	-7.2412818	-4.8417756	-0.2893476
H	-5.9759483	-3.7309656	-1.6471551
H	-8.7407083	-5.7451471	0.9817120
C	-8.9370717	3.5888556	0.9156666
C	-9.1759678	4.6585557	0.0356631
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C	-8.1277690	5.4523375	-0.4022142
H	-10.1904438	4.8465435	-0.3191289
C	-6.5797207	4.1457678	0.9313188
H	-7.4383969	2.5157341	2.0450412
C	-6.8153606	5.2000191	0.0349512
H	-8.3152554	6.2706391	-1.0992243
H	-5.5629879	3.9437572	1.2716155
C	-6.2128197	-5.7535620	0.1093158
C	-5.3503012	-6.5279387	0.4696406
C	-5.7358087	6.0083076	-0.4444687
C	-4.8354441	6.7040498	-0.8670438

C	-4.3509152	-7.4540895	0.9030501
C	-3.0858864	-7.4595273	0.3032770
C	-4.6029327	-8.3854410	1.9219357
H	-2.8470519	-6.7739573	-0.5097060
C	-3.5973954	-9.2672547	2.2944226
H	-5.5791076	-8.4110547	2.4085117
C	-2.3676647	-9.2038022	1.6525106
H	-3.7560447	-10.0058902	3.0799050
H	-1.5429558	-9.8615117	1.9258945
C	-3.7972379	7.5490217	-1.3699095
C	-2.5266097	7.5338213	-0.7824299
C	-4.0192681	8.4271813	-2.4415712
H	-2.3090925	6.8903981	0.0700326
C	-2.9803514	9.2400043	-2.8742880
H	-4.9987403	8.4668898	-2.9205506
C	-1.7486590	9.1632744	-2.2376209
H	-3.1148966	9.9364124	-3.7017496
H	-0.8994407	9.7677340	-2.5553420
N	-1.5375377	8.3246458	-1.2113857
N	-2.1288516	-8.3149896	0.6761656
Pd	0.2972341	8.2999777	-0.2686681
Pd	-0.2972019	-8.3000929	-0.2665687
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C	2.3676429	9.2039644	1.6503219
C	4.3509113	7.4541343	0.9011846
H	2.8470914	6.7738038	-0.5115275
C	3.5973544	9.2675135	2.2922606
H	1.5429268	9.8617159	1.9235829
C	5.3503095	6.5279028	0.4679759
C	4.6028992	8.3856399	1.9199373
H	3.7559816	10.0062667	3.0776366
C	6.2128474	5.7534496	0.1078623
H	5.5790585	8.4113214	2.4065412
C	7.2413396	4.8415718	-0.2905148
C	6.9741321	3.8196797	-1.2162919
C	8.5289794	4.9520749	0.2617804
C	7.9641243	2.9106601	-1.5607577
H	5.9760919	3.7303747	-1.6480867
C	9.5185827	4.0455571	-0.0848441
H	8.7406896	5.7453132	0.9803720
C	9.2422089	3.0034936	-0.9858642
H	7.7450869	2.1015244	-2.2587110
H	10.5098546	4.1182578	0.3652045
C	10.2349860	2.0101612	-1.2537291
C	11.0594723	1.1313109	-1.3962557
C	12.0032398	0.0639244	-1.5064794
C	11.5569651	-1.2585531	-1.7592196

C	13.3629073	0.3152477	-1.3197159
C	12.5090920	-2.2832926	-1.8273274
C	10.1657592	-1.5533242	-1.9047180
C	14.2926874	-0.7256671	-1.3729711
H	13.7127928	1.3247893	-1.1020410
C	13.8638163	-2.0317617	-1.6395250
H	12.1759656	-3.3035044	-2.0249600
C	8.9882011	-1.8372653	-1.9952853
O	15.5771651	-0.3851806	-1.1549508
H	14.5754629	-2.8549524	-1.7027782
C	7.6204177	-2.2363645	-2.1215169
C	7.2909101	-3.2919609	-2.9887231
C	6.5916627	-1.6082292	-1.3804053
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C	5.2665943	-2.0498376	-1.5413638
C	6.8416819	-0.5500303	-0.4468525
H	5.7434143	-4.5458710	-3.8025705
C	4.9601298	-3.0938525	-2.4049321
H	4.4775182	-1.5644801	-0.9644491
C	6.9060382	0.3398024	0.3794883
H	3.9259831	-3.4278285	-2.5074738
C	6.8045797	1.4192708	1.3164378
O	15.5631859	-1.1316076	2.2912469
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C	7.8960838	1.8685331	2.0962083
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C	5.3917143	3.1256243	2.3244328
C	7.7064898	2.9501877	2.9742418
C	9.1921271	1.2650637	2.0187683
C	13.2925217	-1.4749301	1.9185257
C	14.0476327	0.7800847	2.3556700
H	4.4187971	3.6137709	2.4051897
C	6.4707942	3.5739608	3.0882098
H	8.5539321	3.2980338	3.5673390
C	10.3226866	0.8196252	2.0120900
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H	14.8345679	1.5083471	2.5494451
C	12.7295036	1.2198703	2.2808710
H	6.3489760	4.4158159	3.7723552
C	11.6695665	0.3374477	2.0392158
C	10.9197364	-1.9656703	1.5663055
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C	10.0107040	-2.7251351	1.3020902
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C	9.1760307	-4.6586163	0.0371537

C	7.6296117	-3.3483612	1.3682392
C	8.1278225	-5.4524842	-0.4005454
H	10.1905032	-4.8466918	-0.3176009
C	6.5797918	-4.1456113	0.9327111
H	7.4384877	-2.5153424	2.0460738
C	6.8154185	-5.2000594	0.0365718
H	8.3152983	-6.2709391	-1.0973782
H	5.5630625	-3.9435183	1.2729696
C	5.7358580	-6.0084364	-0.4426783
C	4.8354891	-6.7042519	-0.8651232
C	3.7972855	-7.5493024	-1.3678608
C	2.5266534	-7.5340177	-0.7803917
C	4.0193237	-8.4276166	-2.4393944
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H	4.9988003	-8.4673941	-2.9183591
C	1.7487107	-9.1636712	-2.2353641
H	3.1149611	-9.9370253	-3.6993670
H	0.8994913	-9.7681689	-2.5530102
Cl	1.3860741	8.2685892	-2.3645688
Cl	-0.7787743	8.3174169	1.8345740
Cl	-1.3859776	-8.2688377	-2.3625062
Cl	0.7787824	-8.3174115	1.8366848
C	-16.7118395	0.3250462	2.4599652
C	-17.1285464	-0.2812567	1.1325469
H	-16.5511541	-0.4613106	3.2139479
H	-17.4986963	0.9934963	2.8343585
C	-17.5952611	0.7156425	0.0717541
H	-16.2947409	-0.8766673	0.7188294
O	-18.2736622	-1.0769020	1.3048882
C	-16.4980625	1.3701369	-0.7369031
H	-18.1815208	1.5251876	0.5501646
O	-18.4281347	-0.0872142	-0.7323039
C	-18.9304866	-1.1682509	0.0472428
H	-15.9998233	2.1112781	-0.0918198
H	-16.9316833	1.8938564	-1.6047422
C	-18.5678311	-2.4694126	-0.6520441
C	-20.4215653	-1.0031461	0.2789959
H	-18.9337557	-3.3287319	-0.0732933
H	-19.0192146	-2.4986869	-1.6535357
H	-17.4765144	-2.5448725	-0.7595219
H	-20.6163706	-0.0309585	0.7527235
H	-20.9613578	-1.0524673	-0.6765547
H	-20.7949544	-1.8003746	0.9368379
C	16.4980864	-1.3706658	-0.7358770
H	15.9997755	-2.1115571	-0.0905599
H	16.9316837	-1.8946990	-1.6035384

C	17.5953206	-0.7159979	0.0725913
H	18.1815052	-1.5254387	0.5512700
C	17.1286575	0.2812674	1.1330640
H	16.2948941	0.8766029	0.7191552
C	16.7118997	-0.3246022	2.4606629
H	16.5512172	0.4619930	3.2143970
H	17.4987300	-0.9929559	2.8352841
C	18.9306197	1.1678444	0.0474793
C	18.5679257	2.4687691	-0.6522320
H	18.9338471	3.3282875	-0.0737747
H	19.0192875	2.4977164	-1.6537429
H	17.4766057	2.5441760	-0.7597151
C	20.4217051	1.0028469	0.2792574
H	20.6165372	0.0308232	0.7533096
H	20.9614761	1.0518545	-0.6763213
H	20.7950924	1.8003064	0.9368203
O	18.4282783	0.0865367	-0.7317017
O	18.2738220	1.0768945	1.3051643

Charge = 0; multiplicity = 0; (0 imaginary frequencies)
Zero-point correction = 1.813058 (Hartree/Particle)
Thermal correction to Energy = 1.944009
Thermal correction to Enthalpy = 1.944953
Thermal correction to Gibbs Free Energy = 1.623092
Sum of electronic and zero-point Energies = –8062.847995
Sum of electronic and thermal Energies = –8062.717045
Sum of electronic and thermal Enthalpies = –8062.716101
Sum of electronic and thermal Free Energies = –8063.037962

9. SINGLE CRYSTAL X-RAY ANALYSIS

X-ray diffraction-quality single crystals of (*S*,*S*,*P*)-**1** were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the compound. The diffraction data were collected on a Bruker D8 Venture diffractometer equipped with a Photon 100 detector using a Mo radiation source. SHELXT[20] was used to solve the structure. The refinement was performed with SHELX 2018[21] through the WinGX32[22] software using the full-matrix least-squares against F^2 procedure. C–H hydrogen atoms were placed in idealized positions (U_{eg}(H) = 1.2U_{eg}(C) or U_{eg}(H) = 1.5U_{eg}(C)) and were allowed to ride on their parent atoms.

The Br atom of one of the aromatic rings is disordered between two positions due to rotation of the aromatic ring, as shown by a relatively large residual density when only one of the positions (the major one) was considered. An occupancy ratio of approximately 95:5 was found. Therefore, PART, EADP and EXYZ instructions were used to model that disorder. DFIX and DANG restraints were used to model the disordered Br atom in the minor occupancy position.

Summary of the X-ray diffraction measurement and refinement data: Chemical formula, $C_{37}H_{26}Br_2O_4$; *Mr*, 694.40; crystal size [mm^3], 0.655 × 0.442 x 0.064; temperature [K], 100(2); wavelength [Å], 0.71073 (Mo Kα), crystal system, Orthorhombic; space group, *P* 2_1 2_1 2_1; *a* [Å], 9.8523(4); *b* [Å], 10.5545(5); *c* [Å], 29.3310(14); α [°], 90; β [°], 90; γ [°], 90; *V* [Å^3], 3050.0(2); *Z*, 4; ρ_{calcd} [Mg m^{-3}], 1.512; μ [mm^{-1}], 2.698; F(000), 1400; θ range [°],2.377 to 28.768; *hkl* ranges, -13/13, -11/14, -39/39; reflections collected, 34000; independent reflections, 7934; R_{int}, 0.0514; completeness to θ = 25.242°, 99.9%; absorption correction, numerical; refinement method; full-matrix least-squares on F^2; Final *R* indices [$I>2\sigma(I)$], R_1 = 0.0312, wR_2 = 0.0755; *R* indices (all data), R_1 = 0.0335, wR_2 = 0.0767; goodness-of-fit on F^2, 1.036; absolute structure parameter, -0.003(3).

CCDC- 2073558 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/

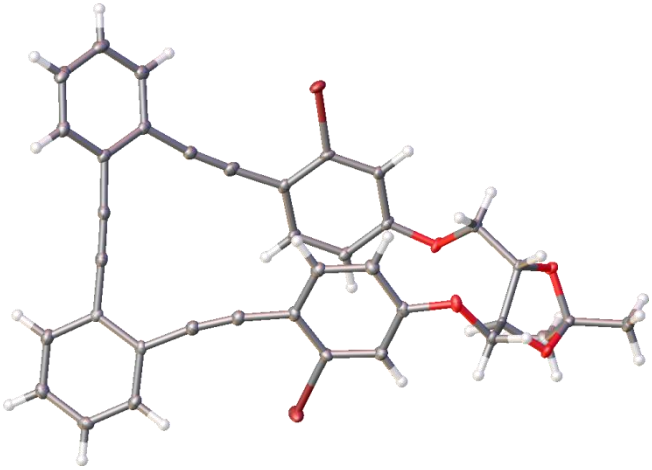

Figure S160. ORTEP-type[18] drawing of the crystal structure of (*S*,*S*,*P*)-**1** showing the ellipsoids at 50% probability. Color coding: C, gray; O: red, H, white; Br, wine. Only the disordered Br in the major position is shown.

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